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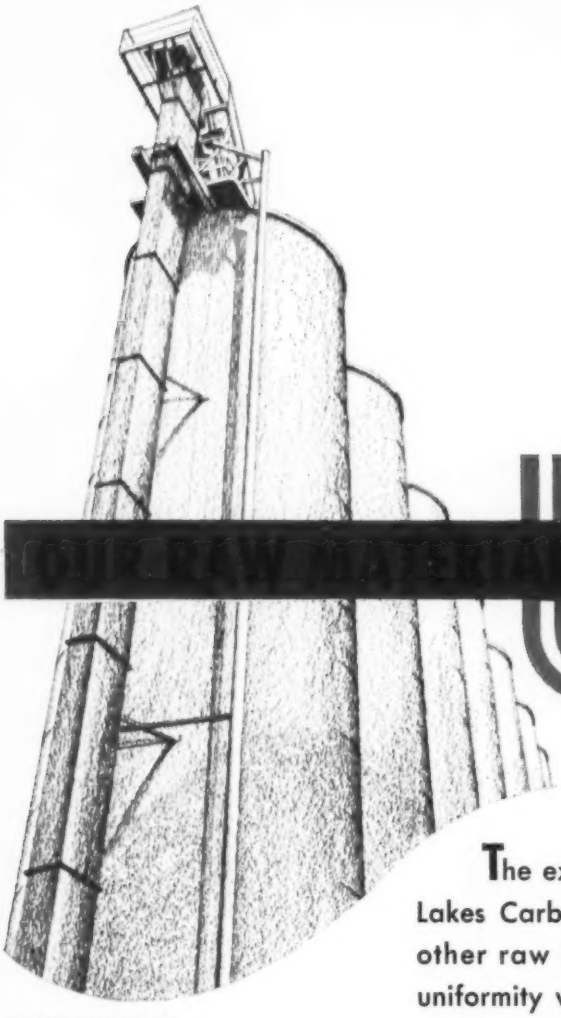

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CONTENTS

Editorial

Recognition to the College Professor 162C

Technical Papers

Punched-Cell Batteries with Polyethylene Glycol Electrolytes. *R. E. Wood* 417
Metal-Water Reactions, III. Kinetics of the Reaction between Thorium and Water Vapor. *B. E. Deal and H. J. Svec* .. 421
Effect of Aluminum Sulfate in the Sulfuric Acid Electrolyte on Anodic Polarization. *R. B. Mason* 425
High Temperature Scaling of Cobalt-Chromium Alloys. *C. A. Phalnikar, E. B. Evans, and W. M. Baldwin, Jr.* 429
Hydrogen Evolution from Dissolving Titanium-Oxygen Alloys in Hydrofluoric Acid and the Constitution of Ti-O Alloys. *M. E. Straumanis, C. H. Cheng, and A. W. Schlechten* 439
Anodic Coprecipitation of Trace Amounts of Manganese and Silver with Lead Dioxide. *J. T. Byrne and L. B. Rogers* 442
Use of Radioactive Mercury to Study the Relation of Mercury to Depreciation of Fluorescent Lamps. *George Burns and Jacob Kastner* 447
Cathodic Reaction of 3,4,5,6-Tetrachloro-*N*-(2-Dimethylaminoethyl)-Phthalimide. *M. J. Allen and J. Ocampo* ... 452
Polarographic Studies in Acetonitrile and Dimethylformamide, III. Behavior of Quinones and Hydroquinones. *S. Wawzonek, R. Berkey, E. W. Blaha, and M. E. Runner* 456
Mechanism of Ozone Formation in the Silent Electric Discharge. *J. C. Devins* 460

Technical Review

The Oxygen Concentration Cell as a Factor in the Localized Corrosion of Metals. *Wilson Lynes* 467

Current Affairs

Candidates for Society Offices—1957–1958 ..... 166C
Acheson Medal Award to R. M. Burns 168C
Further Plans for Cleveland Meeting 168C
Highlights of the Meeting of the Board of Directors 169C
Bylaws of The Electrochemical Society 172C
Division News 171C
Section News 176C
New Members 176C
Personals 177C
ECS Membership Statistics 177C
News Items 178C
Book Reviews 180C
Employment Situation 182C

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Editorial

Recognition to the College Professor

LOUISIANA STATE UNIVERSITY, in 1952, established its Boyd Professorships as a means of extending recognition to its faculty members who acquire national or regional distinction through outstanding achievement in some line of endeavor. In addition to the special title, the appointees receive a higher salary than otherwise would be available for their rank. Our congratulations to LSU! Many universities have a few endowed Chairs to which special appointments are made from time to time. The Boyd Professorships are different in that they are not fixed in number or in ratio between schools or departments. The Administrative Officers are responsible for early recognition of achievement and for making suitable recommendation to the President.

College faculty members can offer distinguished service in many ways and, obviously, the first is through excellent teaching. Many devoted teachers spend long hours keeping abreast of the literature, preparing lectures and other classroom work, conducting well-planned laboratories, becoming acquainted with students and their problems. Such men may do little if any publishable research, never write a textbook. Their distinction may be last to be recognized publicly; they are remembered and respected by hundreds of former students, who have found the way smoothed for graduate and professional schools or for other post-graduate careers.

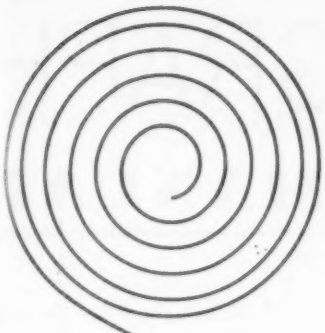
Quicker public recognition is gained by those who carry out, direct, and publish research, write texts and reference books, give lectures at home and abroad, and in general distinguish themselves at an advanced level. In the past, an outstanding scholar might be unknown to any but a few interested colleagues for many years, but this is unlikely today. However, many capable men would no doubt be stimulated to greater efforts if their abilities were accorded early recognition and further opportunity at home.

It is a part of the duties of each College Administration to be aware of the activities of its individual staff members, and to offer encouragement to worthy effort (or censure of delinquency, if need be). Yet we all know of the young Assistant Professor who was mistaken for a graduate student by the Dean; and of the aging Professor whose yellowing lecture notes give him trouble every year because of the errors he made in transcribing them. We remember well the university which encourages its faculty members to go to learned society meetings by offering to pay for first-class one-way transportation.

The universities are naturally troubled by the fact that money is simply not available to pay their teaching staff adequate salaries. It is easier to find money for new buildings than for the people who work in them. It has been pointed out[1] that in 1904 an average professorial salary of $2000 was better than the prevailing average today; that in 1919 the science graduate school professor received about twice the starting industrial salary of the young Ph.D. In order to restore the same relation now, the professor would need close to $15,000. Since the universities must operate on more limited budgets, it is doubly important that their administrative officers explore every method of encouraging and stimulating their teaching personnel.

—CVK

[1] WALTER J. MURPHY, *Chem. Eng. News*, May 14, 1956.



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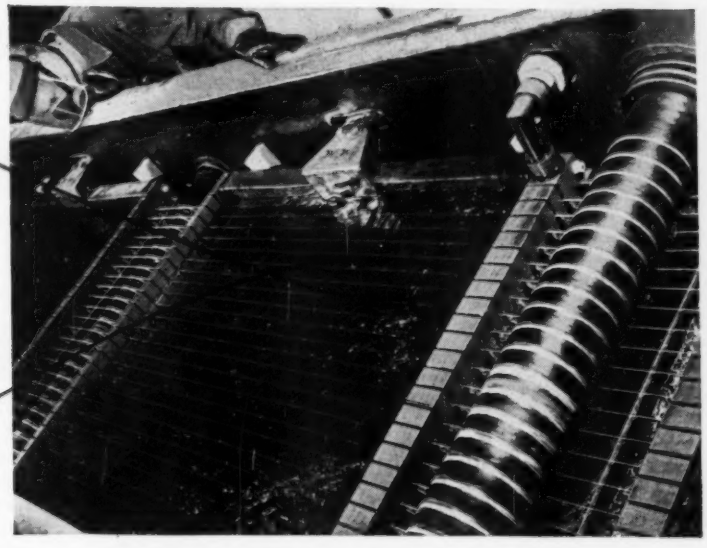

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(2) In those laboratories where a recording instrument is now in use for several determinations, a Model III may be used for each determination, thus releasing the recording Polarograph for research purposes and for establishing the conditions of the routine analyses.
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Punched-cell Batteries with Polyethylene Glycol Electrolytes

Reuben E. Wood

National Bureau of Standards, Washington, D. C.

ABSTRACT

For producing small, high voltage, low current batteries with long shelf lives, it has been found effective to use a waxy electrolyte whose major component is a polyethylene glycol. Results reported here deal with cells having manganese dioxide cathodes, zinc anodes, and, in most cases, a solid electrolyte composed of a polyethylene glycol containing about 5% zinc chloride. A large group of 25-cell batteries have been studied over periods of more than one year. In general, they have shown remarkably little loss of open-circuit voltage. A method of producing dense, strongly adherent, and electrically conductive layers of MnO_2 on conductive plastic films by electrodeposition from a permanganate solution is described. A modified type of cell having a gelled glycol electrolyte is described and discussed briefly.

Since the early days of electrical experimentation the pile type of battery has been appealing because of its simplicity and compact construction. Many embodiments of this kind of construction have been described (1). It is a structure particularly suitable for very small, low current, high voltage batteries. This paper is based on research on such piles, the primary objective of which was to develop a battery of this type with a long shelf life. Secondary objectives were compactness and an extended useful temperature range.

The cells reported on here are related to the Leclanché cell in that they have zinc anodes and manganese dioxide cathodes. They differ fundamentally from the ordinary dry cell as well as from related piles such as those described by Elliott (2) and Reiner (3) in having an electrolyte in which the major constituent is a polyethylene glycol.

Cell and Battery Construction

A typical battery is made as follows. A sheet of zinc about 8 cm wide, 12 cm long, and 0.004 cm thick is degreased by dipping it briefly in 6*N* hydrochloric acid, and rinsing it immediately. Etching promotes adherence of zinc to the waxy polyethylene glycol electrolyte.

A piece of conductive vinyl film is then cut to match the zinc sheet. A piece of filter paper is cut to a slightly larger size than the zinc and plastic sheets. The zinc, conductive plastic, and filter paper sheets are incorporated into a cell as follows.

About 20 g of solid polyethylene glycol is melted and about 1 g of reagent-grade 95% $ZnCl_2$ is dissolved in it. This solution is divided into two approximately equal portions. Into one of these portions is stirred about 10 g of powdered MnO_2. The piece of filter paper is then laid on a hot plate maintained at a temperature somewhat above the melting point of the polyethylene glycol wax, and the hot MnO_2 suspension is painted on one side of it. The other side is painted with the $ZnCl_2$-polyglycol melt which does not contain MnO_2. The filter paper, so prepared, is then taken off of the hot plate and is placed between the zinc and conducting plastic sheets, the conducting plastic facing the MnO_2-coated side of the separator. This sandwich-cell is put back on the hot plate and squeezed with a roller to express excess wax. It is then cooled while being kept pressed together. Next it is put under running water and washed quickly to clean the outside zinc and plastic surfaces. Since these are quite impervious to water it is believed that very little water gets into the cell in this operation except at the edges which, after the sandwich has been wiped dry, are immediately trimmed off.

Disks, either $\frac{1}{4}$ in. (0.635 cm) or $\frac{1}{2}$ in. (1.270 cm) in diameter, are then punched from this sandwich by the use of hardened steel or tungsten carbide punch and die. Twenty-five such cells are then stacked in series in a suitable jig, and, while the battery is held pressed together, the cylindrical surface is lacquered. (A neoprene-base adhesive has also been used and the records so far give no certain indication as to whether this is superior or inferior to lacquer.) The lacquer serves both to seal the edges of the cells and to hold the cells together in the battery. When the lacquer has dried the battery is removed from the jig. Fig. 1 is a photograph of $\frac{1}{2}$ in. and $\frac{1}{4}$ in. 25-cell batteries.

MnO_2 *electrodeposited from permanganate solutions.*—An important modification of this method was the use of electroplated MnO_2 instead of the wax suspension of the MnO_2 powder. It was found that dense, strongly adherent, electrically conductive layers of MnO_2 could be electrodeposited on the conductive plastic films by making them the cathodes in an electrolyte containing about 20 g of $KMnO_4$ and 5 ml of concentrated HNO_3 in a liter of water. Stainless steel anodes and a current density of a few milliamperes per square centimeter were used. The heaviest deposit made was a layer of about 25 mg/cm^2; deposited layers used in batteries were usually from 2 to 5 mg/cm^2.

The surface of these layers usually had the color and texture of slate. The deposit appeared to shrink enough to cause curling when it dried. But it was dense; micrometer measurements on the conducting plastic sheets before and after plating, together with the corresponding weighings gave an apparent density for the MnO_2 of very roughly 5 g/cm^3. Considerations of the increase in resistance of the plating circuit with increase in thickness of the MnO_2 layer gave values for the specific resistance of between

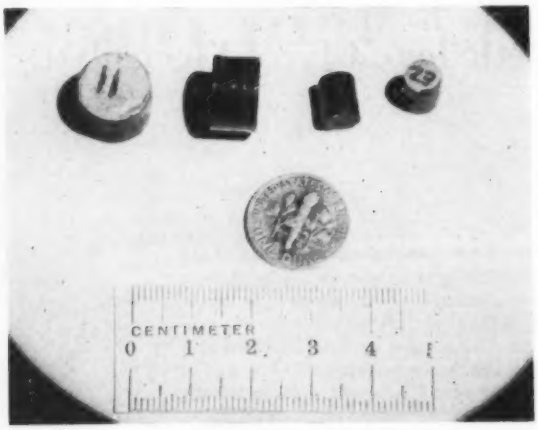

FIG. 1. ½ in. and ¼ in. 25-cell batteries

2×10^5 and 5×10^5 ohm cm. Broken edges of the layer appeared glassy under a binocular microscope; they were reminiscent of the appearance of chips of black obsidian. X-ray diffraction indicated an amorphous structure. Had time permitted it would have been interesting to study more thoroughly this electrodeposition procedure and the properties of the electrodeposited MnO_2 layers. (The symbol MnO_2 has been used broadly; it is recognized that the electrodeposited layer might have a composition departing considerably from that implied by the formula.)

Batteries with cathodes of MnO_2 electrodeposited on the conductive plastic were constructed as previously described except that the separator was impregnated with only the $ZnCl_2$—polyglycol wax mixture, no powdered MnO_2 being used. The sandwich consisted of the zinc sheet, the wax-impregnated separator, and the MnO_2-plated conductive sheet.

Physical and Electrical Characteristics of Batteries

Table I gives characteristics of typical fresh, 25-cell batteries (of the FP separator, 4000 electrolyte type; see notes after Table II). The physical characteristics varied somewhat and the short-circuit currents varied markedly with variations in electrolyte and separator compositions.

Table II is a summary of data on 25-cell batteries. In it the batteries are divided into groups, the members of each group being rather uniform with respect to age and structure. This tabulation includes a large majority of all of the batteries that were made as already described or which involved the modifications indicated in the table. Batteries are excluded from the table for the following

TABLE I. *Physical and electrical properties of representative batteries*

Length	0.85 cm
Weight of ¼ in. battery	1.5 g
Weight of ½ in. battery	6.0 g
Electromotive force	37.5 v
Short-circuit current of ¼ in. battery	3×10^{-8} amp
Short-circuit current of ½ in. battery	3×10^{-7} amp

TABLE II. *Characteristics of polyethylene glycol punched-cell batteries after 1 year or more of shelf life*

Group No.	Number of batteries in group	Electrolyte	Separator	Age range	EMF range	S.C.C. range
Part I*a*: ½ in. (1.270 cm) batteries with powdered MnO_2						
				months	*volts*	*amp* × 10^9
1	4	4000	FP	20	36–37	30–50
2	4	6000	FP	17–18	33–36	25–30
3	8	4000	FP	16	35–37	20–30
4	4	2000	FP	16	35–36	45–60
5	2	4000	Munsing paper	15	33–34	60
6	4	9000w	FP	15	32–34	5
Part I*b*: ½ in. (1.270 cm) batteries with electrodeposited MnO_2						
7	5	4000	R-25-F	13	37–38	140–190
8	5	4000	FP	13	37–38	30–45
9	5	4000	R-45-F	13	21–33	50–110
10	1	4000	Nylon cloth	12	35	80
Part II*a*: ¼ in. (0.635 cm) batteries with powdered MnO_2						
11	1	4000	FP	17	36	5
12	20	4000	FP	17–20	35–37	10–20
13	2	6000	FP	18	31–35	5
Part II*b*: ¼ in. (0.635 cm) batteries with electrodeposited MnO_2						
14	7	4000	R-25-F	13	38–39	50–60
15	13	4000	R-45-F	13	37–38	30–45
16	10	4000	FP	12–13	35–37	10
17	2	4000	Nylon cloth	12	35	25

(a) The number in the "Electrolyte" column refers to the approximate average molecular weight of the polyethylene glycol used. The 9000-w entry means that in this case polyethylene glycol of an approximate average molecular weight of 9000 was used and also that 10% by weight of water was added to the electrolyte. The 9000-w case (Group 6) was the only one in which water was added, although small amounts were doubtless present in all the batteries as an original minor constituent of the battery components and as a result of absorption from the atmosphere during construction of the battery.

(b) Under "Separator", FP means a "qualitative or rough quantitative" grade of filter paper. Actually, two slightly different grades of this type of paper were used during the course of the research but differences shown, if statistically significant at all, seemed too small to justify further subdivision of the table. R-25-F and R-45-F are nonwoven fabrics. These are tough matted sheets with much more open and less homogeneous structure than filter paper. The R means rayon, F is a soft grade and the 25 and 45 are numbers approximately proportional to thicknesses.

(c) Ages are given to the nearest month. Where only one number is given in the "Age range" column, it means that all the batteries in the corresponding group were within ½ month of the age listed.

(d) Values in the emf column represent to the nearest volt measurements made with an electrostatic voltmeter at the time when the batteries were of the ages listed. The electrostatic voltmeter was checked on the day of measurement against a precision, permanent magnet, moving-coil voltmeter.

(e) The numbers in the S.C.C. column when multiplied by 10^{-9} amp are short-circuit currents measured when the batteries were of the ages listed. They were measured with a galvanometer whose sensitivity was 6.0×10^{-9} amp/mm of deflection. Observed values are rounded to the nearest 5.

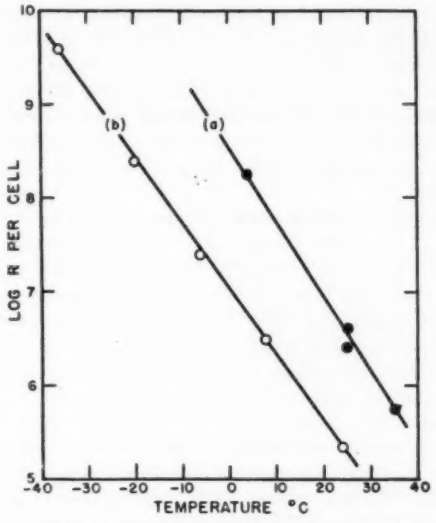

FIG. 2. Cell resistance as a function of temperature. The common logarithm of the resistance in ohms is plotted against the Centigrade temperature. Curve (*a*) is for a wax battery, Curve (*b*) is for a gel battery.

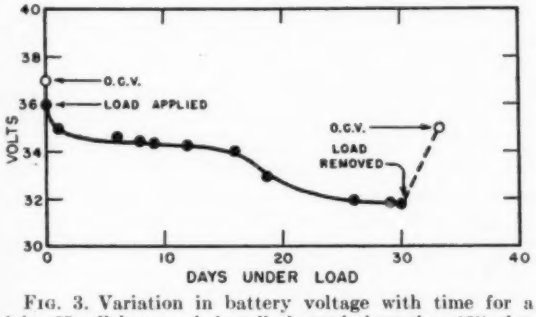

FIG. 3. Variation in battery voltage with time for a $\frac{1}{4}$ in. 25-cell battery being discharged through a 10^{11} ohm load.

reasons: (*a*) several batteries did not contain 25 cells; (*b*) five were given away for testing in another laboratory (*c*) eight were not of the punched-cell type; (*d*) seven involved more radical departure than the others from the described construction and did not seem to yield sufficiently interesting or informative results to warrant their discussion. All of the batteries in Table II are more than a year old. They have been stored during most of their lives at room temperature in desiccators containing silica gel.

Fig. 2(*a*) shows the effect of temperature on the resistance of one of these wax batteries. This battery was about one month old when the measurements were made. Resistances were calculated on the basis of the short-circuit currents at the various temperatures. Fig. 3 shows the performance of a wax battery under a constant load.

DISCUSSION

No study has been made of the electrochemistry of these batteries. A plausible guess would be that anode and cathode reactions can be represented approximately by the following equations, although it should be borne in mind that the oxides of manganese are notable for forming solid solutions or nonstoichiometric compounds:

$$Zn \rightarrow Zn^{++} + 2\,e^- \quad \text{and}$$
$$Zn^{++} + 2MnO_2 + 2\,e^- \rightarrow ZnO \cdot Mn_2O_3$$

The mechanism of conduction in the waxes and, in particular, the importance of water in these wax batteries are also unsettled questions. It is not known whether perfectly anhydrous polyethylene glycol will dissolve and ionize zinc chloride. It would not be expected to be a very good ionizing solvent for ordinary salts. The increase in internal resistance of these batteries during storage in a desiccator may be due to dehydration. Among the interesting possibilities that have suggested themselves in this connection is to try a salt such as tetramethylammonium picrate instead of zinc chloride as the solute, inasmuch as such organic salts are known to be more soluble and more largely ionized than inorganic salts in some organic solvents.

The useful temperature range for these batteries depends on shelf life and current requirements. The shelf life would probably be decreased greatly if the battery were heated above the melting point of the electrolyte, which for electrolyte 4000 (see Table II, footnote *a*) is around 45°C. And, judging from the data represented in Fig. 2(*a*), the lower temperature limit of the useful range for a battery with that electrolyte would be in the neighborhood of 0°C if one takes an arbitrary figure of 10^{-9} amp as the minimum useful current. (Since the internal resistance goes up with age, as indicated by a comparison of Tables I and II, the low temperature limit would also go up.)

The following are some of the implications of the statistics in Table II. Since a very large majority of the batteries have emf's after a year or more of storage which correspond to cell emf's between 1.3 and 1.6 v, it can be concluded that these batteries are not difficult to make and that they have good shelf-life characteristics. At present it is impossible to say whether or not there is a significant difference in shelf life between the $\frac{1}{2}$ in. and the $\frac{1}{4}$ in. batteries. The only difference between these types that has appeared so far is the difference in internal resistance indicated by short-circuit current measurements. It is interesting to note that in old batteries this difference seems to be less than the plate area difference, i.e., the ratio is less than four to one between $\frac{1}{4}$ in. and $\frac{1}{2}$ in. batteries of otherwise similar structure; in fresh batteries, however, (*see* Table I) the ratio is considerably greater than 4 to 1.

There are hardly enough data on electrolytes other than the 4000-type to permit well-founded generalizations about them. The 2000, 4000, 6000, and 9000 w batteries with filter paper separators show internal resistances increasing in that order except for the $\frac{1}{2}$ in. 6000-type batteries which fall into the same short-circuit current range as the comparable 4000-type batteries.

Likewise it seems impossible, at present, to make a relative evaluation of the shelf life and other characteristics of the batteries constructed with electrodeposited MnO_2 as compared with the other type. So far the records show about equal performance for the two types.

There is quite a clear indication with respect to separator materials. Apparently, as might be expected, the more open structured the separator, the lower the internal

resistance. The short-circuit currents from batteries with separators of the most open-structured material used, R-25-F, are greater by a factor of four or five than those of batteries with filter paper separators. A fact that could not have been predicted with assurance is that during more than one year of shelf life, no significant differences in emf have developed between these two groups of batteries. Incidentally no batteries were made which combined the use of powdered MnO_2 and an open-structured separator.

The five batteries in Group 9 have been excluded from consideration in drawing the conclusions stated in the preceding paragraph. The low emf's of that group of batteries cannot be put down to anything recorded about them. The record indicates that they were made in the same way as the ¼ in. R-45-F batteries, all of which give normal emf's. The fact that although they were all made on the same day they were not all punched from the same sandwich only deepens the mystery. However, since every battery of the 25 others with nonwoven fabric separators shows the normal emf, it seems doubtful that the anomalous behavior of Group 9 is significant with respect to the merits of this type of separator. A point of possible practical importance is that batteries in this group showed abnormally low emf's within six weeks after they were made.

Extended Temperature Range

Modifications directed toward producing piles of lower internal resistance and of extended useful temperature range were tried. The results in terms of the shelf-life statistics of a majority of these modified batteries were rather unsatisfactory. They seem, however, sufficiently interesting and, in the case of a few batteries, sufficiently encouraging to warrant a brief presentation.

The modification to be discussed involves the use of ethylene glycol or its lower, liquid polymers instead of the waxy higher polymers. A certain commercially available, synthetic, water-sensitive gum was found which will absorb ethylene glycol and its liquid polymers to form tacky gels which do not melt but retain their stickiness over extended temperature ranges. According to the limited information at present available to the author this gum is a polymeric carboxylic acid.

Punched-cell batteries similar to those described were made up using gelled glycol electrolytes. Paper separators were impregnated generously with a mucilage, a typical composition for which is: 50 ml of 1% aqueous zinc chloride, 7 ml of ethylene glycol or liquid polymer, 2 g of synthetic, water-sensitive gum. Water was evaporated from the separator by putting it on a hot plate kept at, say, 125°C. A sandwich was then made by sticking the separator between a zinc sheet and a sheet of MnO_2-plated conductive plastic, and the disk cells were punched from this sandwich.

Fig. 2(*b*) indicates the results of resistance measurements at various temperatures on one 1¼ in. 22-cell battery of this kind. In thise case, resistances were obtained not from short-circuit currents but from measurements of battery voltages under various known loads. The slope of the curve in Fig. 2(*b*) is roughly the same as that of the curve in Fig. 2(*a*), indicating that the resistance ratio of the two types of cells varies only a little with temperature over the range studied. For these two particular cases, the ¾ in. wax cell has about 50 times the resistance of the ¼ in. gel cell at the same temperature. This implies that the gel cells would have a considerably lower limit to their useful temperature range than the wax cells.

The gel cells can be heated to rather high temperatures with no apparent damage. Two 25-cell batteries were heated for several minutes to temperatures above 100°C while they were being coated with de Khotinsky cement (instead of lacquer). After 11 months these two batteries still have voltages of 30 and 31 v which are, in fact, higher than the voltages of any of the other gel batteries which have stood for comparable lengths of time.

Most of the lacquered gel-type batteries which have been stored in the desiccator have become sticky, a change which has not occurred with the wax-type batteries. The gel batteries sealed with neoprene-base adhesive have not become sticky but bubbles can be seen to have formed under the surface of the coating. All of a considerable sampling of gel-type cells which were never made into batteries but have stood for periods of 10–11 months show voltages close to 1.3.

The facts stated in the two preceding paragraphs strongly suggest that the poor shelf life shown by most of the gel batteries is caused by intercell leakage and not by poor shelf-life characteristics inherent in the cells themselves. Individual cells of this kind, therefore, might be useful (as bias cells, for example) even if they cannot be successfully and simply combined into a very compact battery giving satisfactory performance. However, the comparatively good showing of the de Khotinsky-sealed batteries offers hope that the problem of intercell leakage can be solved and that the relatively low resistance and extended temperature range of the gel-type cells can be incorporated into punched-cell batteries having long and dependable shelf lives.

Acknowledgments

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Metal-Water Reactions

III. Kinetics of the Reaction between Thorium and Water Vapor[1]

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ABSTRACT

An examination of the reaction between thorium metal and water vapor has been made between 200° and 600°C and at water-vapor pressures of 25 to 100 mm Hg. Analyses of the products indicate that ThO_2 and H_2 are the main species formed during the reaction with formation of ThH_2 as a possible side reaction product. Two methods, one gravimetric and the other manometric, were used to determine rates of reaction. During these rate studies, the variables time, temperature, and pressure were examined. Reaction data were found to obey the logarithmic rate law $w = k \log(1 + 0.45t)$. The activation energy was found to have an average value of 6.44 ± 0.75 kcal/mole. From marker experiments it is postulated that inward diffusion of water molecules or a related species is the rate-determining step of the reaction. Other experiments showed that hydrogen diffused into the metal in varying amounts depending on temperature and water-vapor pressure. This hydrogen was evolved when the samples were heated under high vacuum to 1200°C.

Numerous references are available for metal-gas reaction-kinetics studies involving O_2, N_2, and H_2 (1). However, few studies have been reported on metal-water vapor reactions. Because of the increasing importance of thorium and related metals in the field of atomic energy and because of the role water vapor plays in metal corrosion, a program was initiated to study the kinetics of the reaction between thorium and water vapor.

The reaction between thorium and oxygen has been studied by Levesque and Cubicciotti (2) as well as Gerds and Mallett (3). A parabolic rate law was found to fit the data at most temperatures, which is in agreement with data for many metal-oxygen reactions. However, Brodsky and Cubicciotti (4) found that silicon-oxygen reactions obeyed a logarithmic rate law, while Alexander and Pidgeon (5) reported a similar law for the oxidation of titanium by oxygen. Deal and Svec (6) found the reaction between lithium and water vapor to proceed according to a logarithmic rate law as do the reactions of water vapor with calcium (7) and uranium (8).

EXPERIMENTAL

Thorium metal was obtained from the Metallurgical Section of the Ames Laboratory of the A.E.C. in the form of a cast billet. Spectrographic analysis indicated that the total impurities were less than 0.1% occurring principally as C, N, Fe, Be, Ca, and Si. Cylinders of the appropriate dimensions were prepared under the same conditions described in a previous paper concerning lithium-water vapor reaction kinetics (6).

The main reaction between thorium and water vapor proceeds according to the equation

$$Th + 2H_2O = ThO_2 + 2H_2$$

The reactions were followed either by a manometric method in which the amount of evolved gas was measured or a gravimetric method in which the weight gain was measured. The manometric apparatus consisted of a recording manometer (6), a reaction tube placed in a furnace, an inlet for introducing water into the system and controlling its vapor pressure, and a vacuum system consisting of a mercury diffusion pump and a mechanical pump. As hydrogen was evolved by the reaction of water vapor with thorium, its increasing pressure was recorded and converted to the weight of water vapor that had undergone reaction.

The gravimetric method made use of an electromagnetically controlled microbalance modified for simplicity and increased load but based on the design of Edwards and Baldwin (9). The balance beam was a quartz tube suspended from a quartz rod frame. A cylindrical Cunife magnet was mounted axially in this tube. The beam was placed between two coils of wire and its position could be controlled by varying the amount of current flowing in the coils. In principle the balance behaves as a tangent galvanometer. All weight measurements were made by a null method and weights were measured in terms of the amount of current flowing in the coils. The balance was enclosed in an all-glass apparatus which could be evacuated and which included a small furnace in which the thorium cylinder hung during the reaction. Both furnaces used in the manometric and gravimetric studies were controlled by a proportioning furnace-temperature controller (10). A complete description of both systems used in these studies is given in reference (11). In either system, both vapor pressure and thorium temperature could be

[1] Contribution No. 450. This work was performed in the Ames Laboratory of the Atomic Energy Commission, Iowa State College, Ames, Iowa. Other papers in this series have appeared in *J. Am. Chem. Soc.*, **75**, 6052, 6173 (1953). This paper taken from the Ph.D. dissertation of B. E. Deal.

varied independently. Vapor pressures ranged from 25 to 100 mm Hg and temperatures were varied from 200° to 600°C.

For each reaction, a freshly machined thorium cylinder was placed in the appropriate apparatus. The system was evacuated, thorium temperature was adjusted, liquid water was introduced, and water vapor pressure was adjusted to the desired value. Data obtained from either apparatus were converted to weight per unit area of water vapor undergoing reaction.

Results

Examination of the thorium-water vapor reaction products by x-ray diffraction and mass spectrometric techniques indicated that only ThO_2 and H_2 were formed. Three different-appearing oxide coatings were observed, however, depending on the temperature range. Between 200° and 275° a black oxide coating was formed; from 300° to 425° a white or gray coating was observed, and from 450° to 550° the coating was metallic in appearance. From the x-ray diffraction patterns for the three different-appearing reaction-product coatings, it appears that extremely small crystallites were formed at the lower temperatures while, as the reaction temperature became higher, larger and more perfect crystals were formed. No changes in lattice patterns were observed in any of the colored oxides.

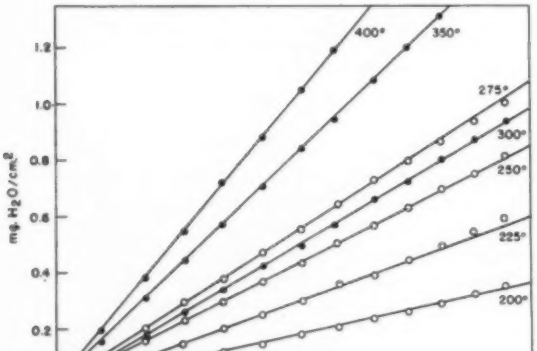

Fig. 1. Logarithmic plot of thorium-water vapor data at 70 mm Hg water-vapor pressure and varying temperatures.

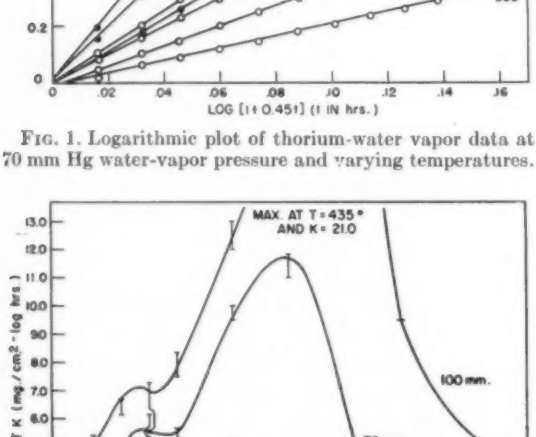

Fig. 2. Effect of temperature on rate constants from thorium-water vapor data.

Since the reaction between thorium and water vapor proceeds with the formation of a surface coating, reaction rate data were expected to fit one of the usual solid-gas rate laws. On plotting the weight of water consumed (in mg per cm² of thorium surface) against appropriate functions of time, a straight line was observed for the logarithmic treatment of the data, while definite curves were evident for the other laws. The value of the constant a in the logarithmic equation $w = k \log [1 + at]$ was empirically determined to be 0.45 as was the case in the Li studies and is the case in current studies with Ca and Sr. Brodsky and Cubicciotti (4) found that 0.4 was the value for this constant in the reaction of silicon with oxygen. Since the value 0.45 was obtained as the average of 0.40 and 0.50, both of which fitted the data equally well, the value found by these workers is the same as the one reported here.

Graphs were prepared for each reaction with mg H_2O/cm² plotted against log $[1 + 0.45t]$, where t is time in hours. Values of the logarithmic rate constants k were obtained from the slopes of the initial part of the curves. Fig. 1 shows plots of typical data for the water-vapor pressure of 70 mm Hg and indicates the temperature dependence between 200° and 400°C. The two different symbols on the graphs indicate two of the reaction-product regions mentioned above. The effect of temperature on rate constants is more clearly observed in Fig. 2, where temperatures are plotted against rate constants at three vapor pressures. These curves each have regions in the temperature ranges 200°–275°, 300°–400°, and 450°–550° which correspond to the different-colored ThO_2 coatings observed on the metal specimens used in the experiments.

The activation energy for the thorium-water vapor reaction was determined from an Arrhenius plot of the data. Fig. 3 shows this plot for two reaction products regions and for three vapor pressures using manometric data. Gravimetric data for 70 mm water-vapor pressure are plotted in Fig. 4 which also includes data for deuterium oxide reactions. A least-squares treatment of the data gives an average value of 6.44 ± 0.75 kcal/mole for the activation energy. Parallel straight lines corresponding to this value have been drawn through the points in Fig. 5 and 6 and it can be seen that all points lie near one of these lines within the experimental error.

The most important relationship showing pressure dependence of metal oxidations is based on solid-gas diffusion phenomena. The general equation

$$k = -Cp^n e^{-b/T}$$

where k is the rate constant, p the pressure, T the absolute temperature, and C, n, and b are constants has been proposed by Barrer (12). The exact mechanism of the reaction determines the value of the constant n.

A definite pressure dependence is observed in Fig. 5 for the reaction between thorium and water vapor at 300°C. In order to get a better idea of the exact order of pressure dependence, idealized rate constants were calcu-

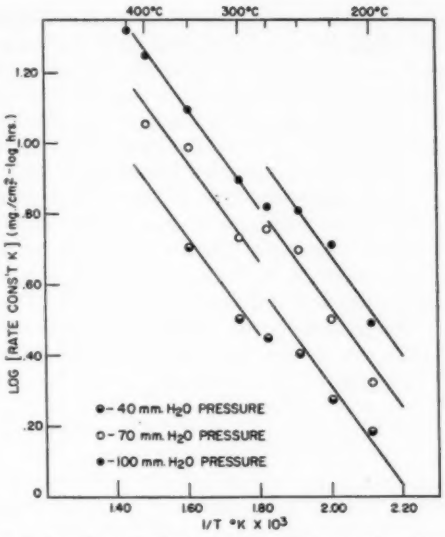

FIG. 3. Log k vs. $1/T$ at varying pressures from thorium-water vapor data.

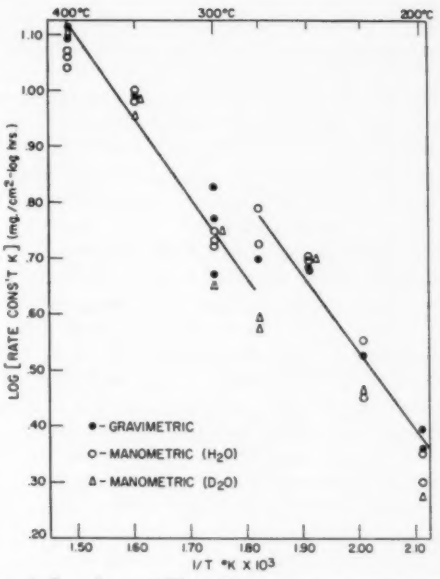

FIG. 4. Log k vs. $1/T$ at 70 mm water vapor pressure comparing manometric and gravimetric experimental procedures.

lated from the straight lines in Fig. 3 and plotted against pressure. The resulting plot showed first order dependence for all temperatures studied. Two equations,

$$k = 31.5pe^{-6440/RT}$$

and

$$k = 21.9pe^{-6440/RT}$$

were obtained for the ranges 200°–275° and 300°–400°, respectively.

Deuterium oxide was also used in a series of Th-water vapor reactions. No significant differences from the H_2O reactions were found in the observed rates. In all cases the reaction products had the same appearance as the H_2O reactions and the same discontinuities appeared in the rate data as is indicated in Fig. 4. Of considerable significance was the observation that the absolute values of rate constants obtained from gravimetric experiments were slightly, but consistently, higher than those obtained from manometric data. However, plotting gravimetric data gave the same activation energy for the reaction, indicating that the difference in absolute values for the rate constants was due to some constant effect.

Since it has been proposed that a logarithmic rate law indicates diffusion of some species in the growing reaction product coat, a pressure dependence on the reacting gas would indicate that diffusion inward of the reacting gas or some related species might be the rate-determining step. In order to determine if there were such an inward diffusion or if thorium ions were diffusing outward, an inert-marker experiment was carried out. It consisted of placing securely a 0.05-in. diameter platinum wire vertically into the side of a thorium cylinder and machining the end of the wire even with the thorium surface. After a typical reaction with water vapor the position of the thorium surface and the end of the platinum marker in relationship to each other were examined microscopically and microphotographs were made. It was observed that the

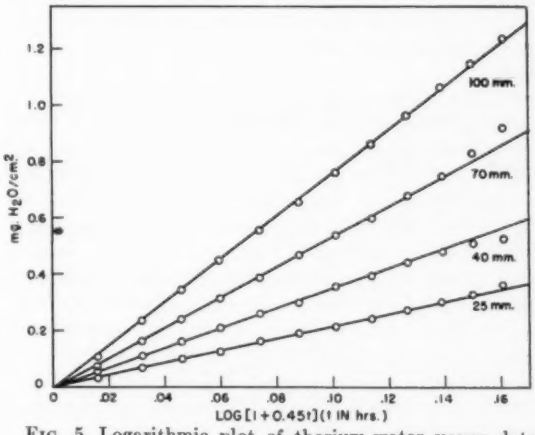

FIG. 5. Logarithmic plot of thorium-water vapor data at 300°C and varying water-vapor pressures.

end of the wire extended well above the thorium-thorium oxide interface, substantiating the possibility of an inward diffusion of some species since, for outward diffusion of thorium ions from within the metal, the end of the Pt wire and the thorium surface should have remained in the same plane.

The microphotographs showed a new phase extending into the bulk of the thorium metal from the Th-ThO_2 interface and along grain boundaries, as well as scattered throughout the bulk of the thorium within the grains. These intergranular and intragranular materials were different in appearance from known oxide inclusions and are believed to be a hydride. The presence of a hydride or dissolved hydrogen would explain the discrepancies in rate constant values obtained in the manometric and gravimetric experiments. Vacuum heating experiments

were carried out to analyze for gases in a thorium cylinder. Various specimens which had been exposed to either D_2O or H_2O vapor were heated to 1200°C and the evolved gas was collected and analyzed. This gas was found to be only hydrogen. It was found that thorium specimens in contact with water vapor contained from 33 to 111 ppm H_2 depending on the history of the specimen. Metal not previously known to be in contact with water vapor contained from 0.6 to 1.1 ppm H_2.

Metallographic examination of the thorium specimens after vacuum heating indicated that the intra- and intergranular phases mentioned above had disappeared completely. These phases then were associated with the evolved hydrogen and were assumed to be a thorium hydride which had decomposed during the heating. While no positive identification was made, from the work of Nottorf and co-workers (13) and the temperature at which the thorium-water vapor reactions were run, the new phases were assumed to be thorium dihydride. Further corroboration of this was obtained by blocking off an area on microphotographs of the interior of the metal specimens and determining the relative areas of the metal and new intragranular phase. After correcting for density differences, calculating the hydrogen content on the basis of dihydride or 3.75 hydride, and comparing with the amount of hydrogen found in a metal specimen from which the outer portion of the metal was removed, good agreement was observed assuming ThH_2 to be the new phase.

In order to determine if the presence of hydrogen gas produced during the reactions affected the values of the rate constant, a palladium diaphragm was employed to remove evolved hydrogen. The Pd diaphragm was in the form of a thimble of metal 0.001 in. thick and heated to 300°C. No differences were observed in rate-constant values. Even in the higher temperature, lower pressure range, where the vacuum heating experiments indicated that relatively large amounts of hydrogen diffuse into the thorium, the weight gain remained the same. These results indicate that a fraction of the hydrogen released during the splitting of HOH molecules diffuses into the metal without first forming molecular hydrogen and that this occurs at or near the Th-ThO_2 interface.

Discussion

Diffusion of some species in the growing reaction product coat has been assumed to control the rate of reaction between thorium and water vapor. The nature of the reaction indicates several possibilities. Water molecules may be diffusing inward, Th ions may be diffusing outward, electrons may be moving outward and hydrogen may be moving in both or either directions. It is possible that a combination of all processes are going on simultaneously.

The ratio of the molecular volumes of ThO_2 to Th is 1.32; thus as the coating thickens it is subject to severe strains and adhesion of the coating is affected. During the oxidation of the metal at constant gas pressure and temperature the various laws may apply consecutively with time depending on the extent of film thickening. These experiments were not designed to observe the linear nature of the initial association of water vapor with the metal. Indeed a parabolic law, which might have been expected when the coating film was still thin enough for the existence of a linear concentration gradient of the diffusing species, was not observed. The main observations were made after the films had apparently thickened enough to be affected by the strains due to the disparity of the molecular volumes involved. This occurred early during the reactions since most of the coatings were only about 0.01 mm thick when the observations were completed. Under these strained conditions, blistering, crazing, or even flaking should have and did occur. For long reaction times the ThO_2 coating actually flaked off irregularly causing unpredictable changes in the reaction rates after flaking began. However, the reaction during the first hour invariably proceeded with an adherent coat and reproducible data were obtained.

Fig. 3 and 4 indicate breaks in the Arrhenius plots of the data. This occurs in the temperature range where the rate also appears to be constant with temperature as indicated in Fig. 4. It is significant that for coatings formed at 250°C x-ray diffractometer tracings are extremely diffuse while those from coatings formed at 350°C are beginning to become sharp. Also the physical appearance of the coating changes from black to opaque gray-white. It is postulated that a change in the dominant rate-determining step takes place somewhere between 250° and 300°C. However, the expected change in activation energy is not evident, probably due to the insensitivity of the experimental procedure to elucidate small effects.

The marker experiments at 250° and 350°C indicate that some species are diffusing inward. However, the gas-oxide interface extended slightly beyond the end of the Pt marker indicating that outward diffusion of some species may also have been possible although this may be explained on the basis of the greater molecular volume of the oxide. This coating is highly frangible, and high power microscopic examination of its surface showed extensive crazing. It is postulated that the observed logarithmic law is due to the diffusion of water molecules through the microscopic fissures in the coating and that these diffusion paths are blocked in a random way due to the layer structure of the coating. This comes about by successive healing and re-cracking of the layers as the coating grows. Reaction takes place at or near the metal-oxide interface. This accounts for the pressure sensitivity observed which is primarily a manifestation of a mass effect. It also explains the deuterium oxide data and the high absorption of hydrogen by the metal when gaseous hydrogen is continuously removed from the reaction vessel. Hydrogen adsorption by massive metal in an atmosphere of pure H_2 is extremely slow compared to that observed in the water vapor reactions.

The decrease in reaction rate at temperatures above about 400°C is similar to a phenomenon observed in the reaction between Ca and water vapor (14). It is postulated that the rate of escape of water molecules from the oxide surface increases in this temperature range thus making fewer molecules available for diffusion through the coat.

From Fig. 4 there is a suggestion that the rate of reaction may become pressure independent beyond 600°C. X-ray patterns of the oxide formed at this temperature are very

sharp while the coating is transparent giving the metallic appearance referred to earlier in this paper. Microscopic examination indicates considerably less crazing. If the logarithmic rate still holds in this temperature region, it is probable that ionic diffusion, through statistically blocked paths, becomes rate determining. It is possible that some other rate law may apply.

Chiotti and White (15) have determined the coefficient of thermal expansion for both Th metal and ThO_2. In the temperature range 0°–1000°C the ratio of the molecular volumes of oxide to metal is 1.34–1.31. Thus, the change in rate of reaction cannot be attributed to any transformations in metal or oxide. The marked crystal growth of ThO_2 at higher temperatures is the most significant evidence that the diffusion medium changes considerably throughout the temperature range included in this study.

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Effect of Aluminum Sulfate in the Sulfuric Acid Electrolyte on Anodic Polarization

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ABSTRACT

Anode polarization measurements have been made over a wide range of concentration of the H_2SO_4 electrolyte. For each concentration of acid, the coating ratio (weight of coating divided by weight of aluminum reacting) was also determined. Aluminum sulfate dissolved in the electrolyte decreased the polarization value, but was only about ⅕ as effective as free H_2SO_4. The presence of aluminum sulfate in the electrolyte had little effect on the coating ratio. Additions of oxalic, glycolic, and tartaric acids had only a small effect on the polarization, but increased the coating ratio and decreased the rate of solution of the oxide coating in the electrolyte in which the coating was formed.

An oxide coating is formed when aluminum is made the anode in a dilute H_2SO_4 electrolyte. Not all of the aluminum that reacts with the electrolyte remains on the surface as Al_2O_3. The electrolyte has some solvent action on the anodic coating. The amount of Al_2O_3 produced depends on the concentration of the electrolyte, temperature, current density, and various other factors (1–4). Under normal operating conditions, the amount of Al_2O_3 on the surface is only about 80% of the theoretical value (5). Either the electrolyte reacts directly with the aluminum to form aluminum sulfate (6) or some of the oxide coating dissolves chemically in the H_2SO_4 to form aluminum sulfate.

As a H_2SO_4 electrolyte is used for the anodic oxidation of aluminum, appreciable amounts of aluminum sulfate are produced and accumulate in the electrolyte. The H_2SO_4 combined with aluminum to form aluminum sulfate is usually spoken of as combined H_2SO_4. The effect of this combined H_2SO_4 on the operational characteristics of the H_2SO_4 electrolyte has been studied in various ways and the results have not been too conclusive or consistent (7).

Some investigators have suggested that aluminum sulfate should be added to H_2SO_4 electrolytes intentionally (8). This is not necessarily considered to be good practice (1) since it is known that the electrical conductivity of the H_2SO_4 electrolyte is decreased by such addition (9).

For the same current density the voltage of the 15% H_2SO_4 electrolytic cell is appreciably less when aluminum sulfate is added to the H_2SO_4 electrolyte without any dilution. In other words, the electrolyte containing aluminum sulfate acts as an electrolyte containing more than 15% H_2SO_4. It is assumed that the aluminum sulfate in the H_2SO_4 electrolyte acts as a certain amount of free H_2SO_4.

Anodic coating of aluminum in a H_2SO_4 electrolyte, in a lead tank at 21.1°C (70°F), required 16 v to give a current density of 12 amp/ft². Most of the voltage drop across the cell is from the aluminum anode to the electrolyte and usually amounts to about 13 v. To study the anode reaction it is better to consider the voltage drop from the aluminum anode to that of an auxiliary electrode since the voltage drop through the electrolyte and the lead cathode may vary considerably depending upon the size of the tank and other factors not generally controlled. In this paper, the voltage drop from the aluminum anode to the auxiliary electrode is called anodic polarization.

It has been found that the anodic polarization increases only about 1 v upon coating for 30 min, while the oxide coating increases from a very thin film to a relatively thick coating. Therefore, most of the polarization occurs across the very thin barrier layer which is about 150Å thick. In this narrow region, considerable heat is developed that must be removed rapidly. The heat developed will be greater as the polarization voltage increases. Poor agitation allows the electrode to heat up and polarization decreases. For reproducible results, it is imperative that sufficient agitation be used to give the maximum polarization values.

In the experiments to be described, polarization measurements were made over a wide range of concentration of H_2SO_4. For each concentration of acid, the coating ratio (weight of coating divided by weight of aluminum dissolved) was also determined. Aluminum sulfate, as well as other substances, was added to H_2SO_4 to determine the effect on polarization, coating ratio, and solubility of the aluminum oxide coating in the H_2SO_4 electrolyte.

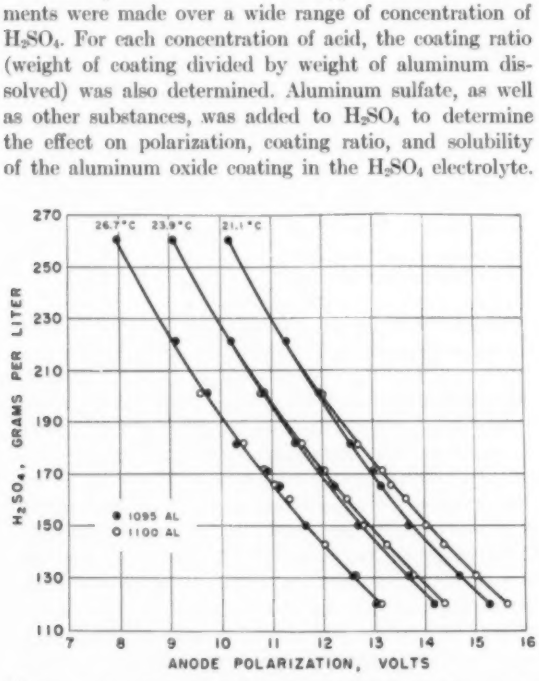

FIG. 1. Anode polarization as affected by changes in H_2SO_4 concentration.

EXPERIMENTAL PROCEDURE

Various H_2SO_4 electrolytes were prepared by weighing out the required amount of analyzed concentrated H_2SO_4 and diluting in a volumetric flask. The density of the diluted electrolyte was checked by means of a 5 cc glass thermometer-plummet and an analytical balance. Addition agents were usually added to the H_2SO_4 before diluting to the final volume and the concentration expressed as grams per liter. However, in one series of experiments, increasing amounts of aluminum sulfate with 18 molecules of water of crystallization were added to a given volume of 15% H_2SO_4. In this case, the acid was diluted by the water of crystallization. The concentration of used solutions was periodically checked by chemical analysis.

The prepared electrolyte was held in a two liter beaker containing a lead cooling coil which also served as the cathode. A motor-driven glass stirrer was used to furnish adequate agitation of the electrolyte in order to remove the heat developed at the anode surface. Aluminum anodes about 5.1 cm x 7.6 cm (exactly 12 in.² of surface) with a narrow tab coated with an acid resist were anodically coated using a current density of 1.3 amp/dm² (12 amp/ft²) at 21.1°, 23.9°, and 26.7°C (70°, 75°, and 80°F). Polarization was determined after 10-min coating time by means of a small auxiliary electrode of lead peroxide placed near the surface of the anode and a high resistance voltmeter (5000 ohms/v).

To determine the coating ratio, the aluminum anodes, 5.1 cm x 7.6 cm (2 in. x 3 in.) were cleaned, weighed, and then suspended in the electrolyte by means of tantalum clips and oxide coated for 30 min at a current density of 1.3 amp/dm² (12 amp/ft²) at the given temperature. The specimens were removed, washed, dried, and weighed. The oxide coating was then removed in a hot phosphoric-chromic acid solution and the specimen again weighed. From the weight of coating and the weight of metal dissolved, the coating ratio was determined. For the solubility determinations, specimens of aluminum sheet were anodically coated for 30 min and then suspended in the various electrolytes which were uniformly agitated. The oxide coated specimens were periodically removed, dried, and weighed to determine the rate at which the anodic coating dissolved in the electrolyte.

EXPERIMENTAL RESULTS AND DISCUSSION

Using an auxiliary electrode of lead peroxide, anode polarization measurements were made in H_2SO_4 electrolytes varying in concentration from 120 g/l to 260 g/l. The 1100 and 1095 aluminum sheet specimens having a surface area of exactly 77.4 cm² (12 in.²) were used for making the polarization measurements at 21.1°, 23.9°, and 26.7°C (70°, 75°, and 80°F) in the various concentrations of H_2SO_4, a current density of 1.3 amp/dm² (12 amp/ft²) being used for each determination. Data for these polarization values are shown graphically in Fig. 1.

The polarization value for the high purity metal is lower than that for the 1100 alloy, especially at lower temperatures and concentrations of acid. However, this difference in polarization value for the 1095 and 1100 alloy decreases as the temperature is raised or as the concentration of the acid is increased. Polarization values for aluminum of two

TABLE I. *Effect of combined H_2SO_4 on anode polarization*

Electrolyte containing	Temp.	Anode* polarization	Effective H_2SO_4	CAE†
	°F	v	g/l	%
164.5 g/l free H_2SO_4	70	12.45	183	19.7
+ 93.8 g/l combined H_2SO_4	75	11.35	184	20.8
	80	10.30	183	19.7
139.1 g/l free H_2SO_4	70	13.85	148	18.8
+ 47.3 g/l combined H_2SO_4	75	12.85	148	18.8
	80	11.85	147	16.7

* Anode polarization determined with PbO_2 auxiliary electrode. 1095 anode material.

† Per cent combined acid effective (acting as free H_2SO_4).

different purities are practically equal at higher temperatures and concentrations of acid.

Instead of plotting the polarization voltages of the anode, it is also possible to plot the total voltage of the lead-aluminum cell against the concentration of the H_2SO_4. Curves for total volts are practically identical with the curves of Fig. 1 except for the voltages. Since the total voltage is sometimes influenced by variations in cathodic polarization, only the curves for anodic polarization have been reported since they are considered to be more easily reproduced.

When aluminum sulfate is added to a H_2SO_4 electrolyte, the anode polarization decreases just the same as if a small amount of H_2SO_4 had been added. However, only a small fraction of the combined H_2SO_4 in the aluminum sulfate acts as free acid. The two electrolytes of Table I having both free and combined acid are used to illustrate this. Polarization values were used to determine from Fig. 1 the effective H_2SO_4 concentration in grams per liter. The per cent of combined acid that is effective as free acid was calculated by subtracting the free H_2SO_4 from the effective H_2SO_4 and then dividing by the combined acid. In round numbers, only about $\frac{1}{5}$ of the combined H_2SO_4 acts as free acid.

In some related experimental work, it has been noted that the voltage of the lead-aluminum cell remained constant as varying amounts of crystalline aluminum sulfate were added to a given volume of 15% H_2SO_4. This work was carefully repeated with 1095 aluminum at 21.1°, 23.9°, and 26.7°C (70°, 75°, and 80°F) using the sensitive voltmeter for the anodic polarization and the total voltage measurements. For each temperature, the voltage remained constant to within about 0.1 v even though the additions of crystalline aluminum sulfate varied from 50 g to 300 g to 1 liter of 15% H_2SO_4. The water in the crystals of aluminum sulfate was sufficient to dilute the 15% H_2SO_4 and counteract the effect of the combined acid.

After determining the densities of the various solutions, it was possible to calculate the free and combined H_2SO_4 in grams per liter as well as the per cent of combined acid which is effective. These results are recorded in Table II. Only about 18% of the combined H_2SO_4 is effective as free acid in changing the anodic polarization.

Two methods are now available for determining the active concentration of the H_2SO_4 bath. The amount of free and combined H_2SO_4 can be determined by chemical analysis. The active concentration is then obtained by adding 18% of the combined acid to the free acid. The bath may be restored to its original concentration and operating conditions by adding fresh H_2SO_4 in an amount equal to the difference between the original concentration and the active concentration as calculated above.

Another way is to determine the polarization voltage of a standard sample in a small external cell or in an immersion cell in the production bath and find the active concentration of the H_2SO_4 from the curves in Fig. 1. The amount of fresh acid required can be determined readily by subtracting the active concentration from the desired concentration.

The practice of keeping the amount of free acid constant in the H_2SO_4 bath is not recommended. About $\frac{1}{5}$ of the combined acid (as aluminum sulfate) acts as free acid and, when the actual amount of free acid is kept constant, the active concentration becomes higher as the concentration of aluminum sulfate increases. Usually the 15% H_2SO_4 bath is discarded after about 20 g of aluminum per liter have been dissolved. At this stage, a precipitate of aluminum sulfate may form at the lower temperatures.

Coating Ratios

In Fig. 2, the coating ratio values at 30 min have been plotted against the concentration in grams per liter of the H_2SO_4 electrolyte. The high purity metal (1095) gives the higher coating ratio values. The coating ratio values are straight line functions of the concentration of the acid. The curves at 21.1° and 23.9°C (70° and 75°F) are nearly parallel, but at 26.7°C (80°F) the coating ratio values fall off more rapidly as the concentration of the acid increases.

To show the effect of aluminum sulfate dissolved in the H_2SO_4 electrolyte on the coating ratio, the results of

TABLE II. *Calculation of free and combined H_2SO_4*

Electrolyte		Equivalent combined H_2SO_4	Density at 25°C	Weight	Volume	Free H_2SO_4	Combined H_2SO_4	%CAE*
1000 ml H_2SO_4 + $Al_2(SO_4)_3 \cdot 18H_2O$								
g/l	g				ml	g/l	g/l	
164.3	—		1.0992	1099.2	1000.0	164.3	0	—
164.3	50	22.08	1.1216	1149.2	1024.6	160.4	21.6	18.3
164.3	100	44.15	1.1430	1199.2	1049.1	156.6	42.1	18.3
164.3	200	88.31	1.1827	1299.2	1098.5	149.6	80.4	18.3
164.3	250	110.39	1.2008	1349.2	1123.6	146.2	98.2	18.4
164.3	300	132.46	1.2181	1399.2	1148.7	143.0	115.3	18.4
164.3	350	154.54	1.2349	1449.2	1173.6	140.0	131.7	18.4

* Per cent combined acid effective (acting as free H_2SO_4).

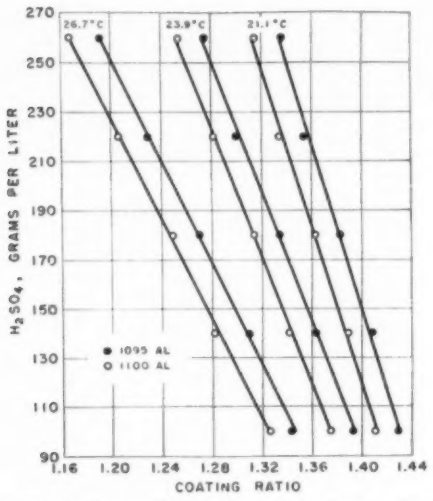

FIG. 2. Coating ratio varying with changes in H_2SO_4 concentration.

TABLE III. *Effect of aluminum, magnesium, and manganese sulfates on the coating ratio*

No.	Electrolyte	Temp °F	Temp °C	Coating ratio 1100 Al	Coating ratio 1095 Al
1	160 g/l H_2SO_4	70	21.1	—	1.391
2	160 g/l H_2SO_4	70	21.1	1.374	1.392
	50 g/l $Al_2(SO_4)_3 \cdot 18H_2O$	75	23.9	1.322	1.346
		80	26.7	1.267	1.288
3	160 g/l H_2SO_4	70	21.1	1.375	1.394
	100 g/l $Al_2(SO_4)_3 \cdot 18H_2O$	75	23.9	1.325	1.347
		80	26.7	1.265	1.286
4	160 g/l H_2SO_4	70	21.1	1.376	1.395
	200 g/l $Al_2(SO_4)_3 \cdot 18H_2O$	75	23.9	1.329	1.347
		80	26.7	1.267	1.292
5	160 g/l H_2SO_4	70	21.1	—	1.394
	100 g/l $MgSO_4 \cdot 7H_2O$	75	23.9	—	1.349
		80	26.7	—	1.289
6	160 g/l H_2SO_4	70	21.1	1.377	1.394
	40 g/l $MnSO_4 \cdot 2H_2O$	75	23.9	1.328	1.345
		80	26.7	1.265	1.286

All samples oxide coated for 30 min at 12 amp/ft² (1.3 amp/dm²).

TABLE IV. *Effect of other acids on the coating ratio*

No.	Electrolyte	Temp °F	Temp °C	Coating ratio 1100 Al	Coating ratio 1095 Al
1	160 g/l H_2SO_4	70	21.1	1.407	1.420
	40 g/l Glycolic	75	23.9	1.366	1.386
		80	26.7	1.316	1.336
2	160 g/l H_2SO_4	70	21.1	1.406	1.423
	40 g/l Oxalic	75	23.9	1.368	1.387
		80	26.7	1.324	1.347
3	160 g/l H_2SO_4	70	21.1	1.395	1.411
	40 g/l Tartaric	75	23.9	1.349	1.368
		80	26.7	1.298	1.322
4	160 g/l H_2SO_4	70	21.1	1.370	1.386
	40 g/l CrO_3	75	23.9	1.321	1.342
		80	26.7	1.260	1.280
5	160 g/l H_2SO_4	70	21.1	1.307	1.320
	40 g/l H_3PO_4	75	23.9	1.194	1.213

All samples oxide coated for 30 min at 12 amp/ft² (1.3 amp/dm²).

Table III have been recorded. It would appear that the presence of appreciable amounts of aluminum sulfate has only a very small effect on the coating ratio. Other sulfates such as magnesium or manganese behave like aluminum sulfate.

Various acids were added to the H_2SO_4 electrolyte and the coating ratio values for 30-min coatings are shown in Table IV. The greatest increase in coating ratio was ob-

TABLE V. *Rate of solution of oxide coatings*

No.	Electrolytes used for coating*	Electrolyte used for dissolving†	Time suspended	Coating dissolved
			min	*g*
A	165 g/l H_2SO_4	165 g/l H_2SO_4	20	0.0147
	100 g/l		40	0.0321
	$Al_2(SO_4)_3 \cdot 18H_2O$		60	0.0514
			80	0.0754
B	174 g/l H_2SO_4	165 g/l H_2SO_4	20	0.0148
			40	0.0322
			60	0.0515
			80	0.0746
C	165 g/l H_2SO_4	165 g/l H_2SO_4	20	0.0140
			40	0.0301
			60	0.0484
			80	0.0704
D	165 g/l H_2SO_4	165 g/l H_2SO_4	20	0.0141
	100 g/l	100 g/l	40	0.0295
	$Al_2(SO_4)_3 \cdot 18H_2O$	$Al_2(SO_4)_3 \cdot 18H_2O$	60	0.0481
			80	0.0699

* Samples of 1095 aluminum having 12 in.² (77.4 cm²) of surface were oxide coated for 30 min at 12 amp/ft² (1.3 amp/dm²) and 70°F (21.1°C).

† Temperature 70°F (21.1°C) with good, uniform agitation.

TABLE VI. *Rate of solution of oxide coatings in mixed electrolytes*

No.	Coated* and suspended in same electrolyte	Time suspended	Coating dissolved
		min	*g*
1	160 g/l H_2SO_4	20	0.0144
		40	0.0303
		60	0.0487
		80	0.0714
2	160 g/l H_2SO_4	20	0.0148
	40 g/l CrO_3	40	0.0310
		60	0.0516
		80	0.0749
3	160 g/l H_2SO_4	20	0.0421
	40 g/l H_3PO_4	40	0.1009
		60	0.1736
		80	0.2172
4	160 g/l H_2SO_4	20	0.0071
	40 g/l Oxalic	40	0.0140
		60	0.0226
		80	0.0309
5	160 g/l H_2SO_4	20	0.0099
	40 g/l Tartaric	40	0.0214
		60	0.0327
		80	0.0481
6	160 g/l H_2SO_4	20	0.0094
	40 g/l Glycolic	40	0.0190
		60	0.0302
		80	0.0421

* Samples of 1095 aluminum having 12 in.² (77.4 cm²) of surface were oxide coated for 30 min at 12 amp/ft² (1.3 amp/dm²) and 70°F (21.1°C).

tained with oxalic acid addition. Glycolic and tartaric acid additions were nearly as good. Chromic and phosphoric acids actually decreased the coating ratio, acting as if more free H_2SO_4 had been added.

Solubility of Coatings

Thirty-minute coatings on 1095 alloy were prepared in the various electrolytes and the rate of solution determined in the electrolytes indicated in Table V.

Aluminum sulfate acts in two ways in the H_2SO_4 electrolyte. The effective acid concentration is increased and, as a consequence, a more readily soluble coating is formed. On the other hand, the presence of aluminum sulfate in the electrolyte retards the chemical solution of the coating. These two effects of aluminum sulfate apparently just counteract each other when a coating ratio determination is made.

An electrolyte containing 165 g/l H_2SO_4 and 100 g $Al_2(SO_4)_3 \cdot 18H_2O$ is equivalent to 174 g/l H_2SO_4. Coatings made in these two electrolytes dissolve at the same rate in 165 g/l H_2SO_4 (see A and B, Table V). They also dissolve at a somewhat slower rate in the H_2SO_4 electrolyte containing aluminum sulfate (see D, Table V). A coating made in a more dilute electrolyte (C, Table V) dissolves at a slower rate.

Data in Table VI have been selected to show how certain acids other than free or combined H_2SO_4 affect the rate at which the oxide coating dissolves. The samples of 1095 aluminum were oxide coated for 30 min at a current density of 1.3 amp/dm² (12 amp/ft²) at 21.1°C (70°F) and tested in the electrolyte indicated. The area of each panel was 77.4 cm² (12 in.²).

Of particular interest are the additions of oxalic, glycolic, and tartaric acids which materially decrease solution rates. These are the same substances which increased the coating ratio values.

Summary

Only about 18% of the combined H_2SO_4, as $Al_2(SO_4)_3$, acts as free acid in the H_2SO_4 bath where voltage of the Pb-Al cell is concerned. A method has been suggested for controlling the active concentration of the H_2SO_4 electrolyte by anodic polarization measurements.

No marked change in coating ratio was noted as aluminum sulfate increased in concentration in the bath. The rate of solution of the anodic coating is decreased by the presence of $Al_2(SO_4)_3$. Additions of oxalic, glycolic, or tartaric acids appreciably increased the coating ratio and decreased the rate of solution of the anodic coating in the electrolyte.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1957 JOURNAL.

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High Temperature Scaling of Cobalt-Chromium Alloys

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ABSTRACT

Scaling rates and scale compositions of Co-Cr alloys were determined in the temperature range 900°–1200°C. At any given temperature the scaling rate increased with low chromium additions, then dropped precipitously with further additions reaching a minimum at about 25% chromium. Thereafter the scaling rate again increased approaching the scaling rate of Cr as the upper limit. Above a critical concentration of about 25% chromium, the scale consisted exclusively of Cr_2O_3. Below this critical concentration, complex scales consisting of the oxides of both cobalt and chromium were formed. The best scaling resistance was associated with a scale consisting predominantly of Cr_2O_3, not spinel. Schematic isothermal sections of the deduced Co-Cr-O phase diagram were applied as an aid in interpreting the scaling behavior.

The scaling behavior of Co-Cr alloys has been studied only once to date, by Preece and Lucas (1). They report single values of weight increase for 50 hr exposure in a simulated gas-turbine atmosphere at 800°–1200°C for alloys containing up to 40% chromium. Their data indicate a sharp rise in weight increase for 10% additions of chromium to cobalt with a subsequent drop for 25% additions and again a rise for 40% additions. In view of the erratic weight increases vs. temperature relationship which these authors reported for pure cobalt (1), computing scaling

TABLE I. *Crystal structure and stability of* Co *and* Cr *and their oxides and nitrides*

Metal or compound	Crystal structure	Lattice constant, A		Stability range °C	Remarks
		a_0	c_0		
Pure metals (4–14)					
Cobalt	β: C. P. Hex.	2.51	4.07	Up to 430	Cubic-to-hexagonal transformation occurs at 388° on cooling.
	α: FCC	3.54		430 to at least 1100	Possible transformation to a hexagonal form at about 1120°
Chromium	BCC	2.885		Up to at least 100 below melting pont	Various structure modification when electroplated.
Oxides (1–3, 12, 14–19)					
CoO	FCC	4.260		Up to 1723	Brown or dark gray, metal-deficit.
Co_3O_4	Cubic (spinel)	8.11		Up to 920	Black
Co_2O_3	Hexagonal	4.64	5.75	Up to 367	Black-gray
CrO	Unknown				Black
Cr_2O_3	Hex. (rhombohedral)	5.38 (α = 54.83°)		Up to 1990	Can exist in several color modifications. Most common—green.
CrO_2	Tetragonal			Up to 300	Brown-black
Cr_2O_5	Unknown				
Cr_3O_8	Unknown				
CrO_3	Orthorhombic			Up to 196	Red
$CoO \cdot Cr_2O_3$	Cubic (spinel)	8.34			
Nitrides (11, 12, 14, 30–32)					
Co_3N	Hexagonal			Up to 380	
Co_2N	Hexagonal			Unstable	
Co_3N_2	Amorphous			Unstable	
CrN	NaCl-cubic			Up to 930	Black
β-Cr_2N	Hexagonal	2.76	4.45	Up to at least 1200	Gray-black

rates from their single values for the alloys is unjustifiable. Indeed, it is not possible to tell if the alloys scale in accordance with the parabolic rate law.

The lack of data on the scaling behavior of Co-Cr alloys in air makes a study of this alloy system an attractive one for a number of reasons. First, cobalt-base alloys containing chromium are of vital interest as high temperature components. Second, these alloys provide a test of Wagner's lattice defect theory (2) which predicts that the addition of a high valency solute (chromium) to a low valency solvent (cobalt) will result in an increase in the scaling rate of the solvent metal. Third, it is of interest to determine whether the other features observed in the scaling of comparable Ni-Cr alloys (3) (two parabolas at those compositions where the nature of the scale changes from solvent oxide to spinel, the formation of spinel at certain alloy compositions, etc.) are to be found.

As part of this investigation, a study of the scaling behavior of the two pure component metals was also undertaken. Since both oxygen and nitrogen may enter in the attack of air on these metals, a summary of the crystal structures of the possible oxides and nitrides is given in Table I.

Material and Procedure

One-inch diameter ingots of pure cobalt and five Co-Cr alloys (8.85, 12.25, 25.57, 38.33, and 48.50 wt % chromium) were prepared by induction melting electrolytic stock (99.9% pure) in zircon crucibles under an argon atmosphere. The top and bottom portions of each ingot were cropped and the remaining section annealed at 2200°F for ½ hr, hot forged at 2000°–1800°F to a ¼ in. diameter rod, and homogenized at 2200°F for 3 hr in a helium atmosphere. The alloy with 48.5% chromium could not be worked due to its extreme brittleness, and was processed simply by annealing at 2000°F for 24 hr in a high vacuum (10^{-5} mm Hg). Slices approximately $\frac{1}{16}$ in. thick were cut from the bars, surface ground,[1] metallographically polished through 3/0 paper, and washed with methanol prior to continuous scaling runs.

Pure chromium specimens were made by electroplating chromium on one side of an oxygen-free high conductivity copper sheet. The thickness of the chromium after stripping from the copper sheet ranged from 0.025 to 0.030 in. Before polishing and subsequent scaling, 1 in. square samples were heated at 400°C for 4 hr to drive off hydrogen gas which was entrapped in the metal as a result of the electroplating operation.

Each specimen was scaled in air by suspending it in a resistance-wound vertical tube furnace from one arm of a magnetically damped chainomatic balance (sensitivity 0.1

[1] Specimens of the 48.5% Cr alloy showed grinding checks. Attempts to obtain specimens from a 63% Cr alloy were unsuccessful due to shattering in the grinding operation.

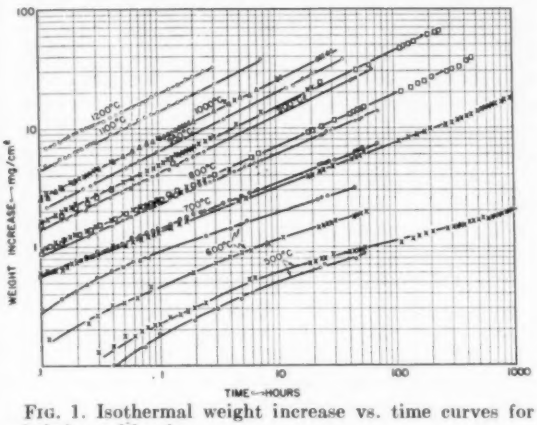

FIG. 1. Isothermal weight increase vs. time curves for cobalt heated in air.

mg). Continuous weight measurements were taken from the moment the specimen was inserted in the furnace.

Scale products formed during oxidation were identified at room temperature by x-rays. Whenever a multilayered scale was formed and wherever possible, scale layers were separated and x-rayed individually using powder samples. When the layers could not be separated cleanly, the individual layers could be identified in some instances by x-raying the scale surface before and after grinding off the outer layer; otherwise, the total scale conglomerate was x-rayed using powder samples.

SCALING BEHAVIOR OF COBALT

The weight increase vs. time data on a log-log scale are shown in Fig. 1. The parabolic law is followed between 500° and 1200°C, with the exception that from 500° to 800° the parabolic law is obeyed after an initial deviation time during which the reaction proceeds at a higher rate. Parabolic scaling constants, from slopes of weight increase squared vs. time, are plotted logarithmically as a function of the reciprocal of absolute temperature in Fig. 2, along with results from the literature. The break in the Arrhenius plot at about 700°C confirms previous investigations (21, 22).

Gulbransen and Andrew's (22) results made an interesting comparison since they studied the scaling behavior of both hexagonal (cold worked) and cubic (annealed) cobalt in oxygen (P_{O_2} = 76 mm Hg) from 200° to 700°C for 2 hr. The hexagonal form was found to oxidize more rapidly than the cubic form. They found that both forms of cobalt oxidized according to the parabolic rate law after an initial deviation, and calculated the scaling constant in the time interval of 1–2 hr. However, the present investigation indicates that from 500° to 800°C this time interval of 1–2 hr is still in the range where the oxidation rate is proceeding faster than the parabolic law would predict and that the scaling rate is somewhat higher than either form of cobalt used by Gulbransen and Andrew[2]

[2] These investigators also found that their high purity nickel oxidized at a slower rate than high purity nickel of other investigators (36). It would seem, then, that differences in experimental techniques (and possibly atmosphere) and not purity of metal cause the difference in scaling rate.

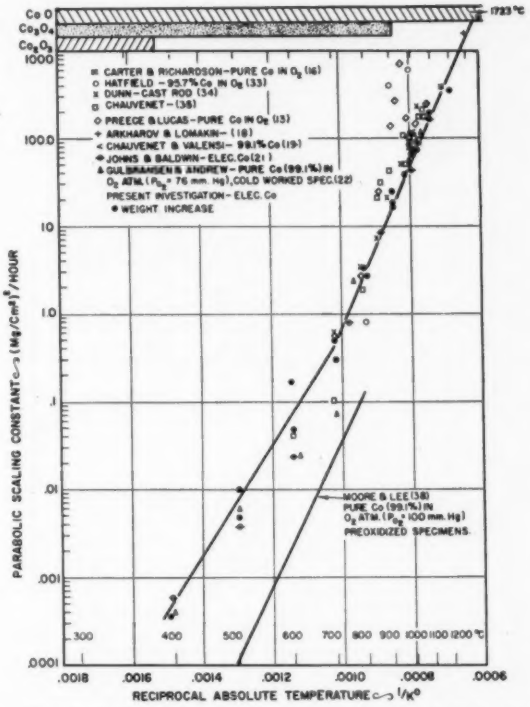

FIG. 2. Arrhenius plot of reaction rate for cobalt heated in air.

(*see* Fig. 3). It is interesting to note that rate constants calculated for 400°–1200°C for the time interval of 1–2 hr can be fitted to a single straight line in an Arrhenius plot, Fig. 3.

The precipitous changes in the oxidation rate of cobalt reported by Preece and Lucas (1) from 800° to 1075° have not been confirmed. Strangely enough, however, the high oxidation rates observed by these investigators at 900° and 950° (*see* Fig. 2) agree well with those reported by Hatfield (33) at these same temperatures, yet the latter used rather impure cobalt (95.7%) in his studies. As pointed out by Kubaschewski (11) the presence of an appreciable amount of high valency impurities in a metal which forms a metal-deficit oxide, of which CoO is an example,[3] may increase the scaling rate.

The much slower rates of oxidation observed by Moore and Lee (38) at low temperatures can again be attributed to the use of preoxidized specimens, as previously noted with nickel (36).

The scale found on cobalt was double-layered (*see* Fig. 8). At temperatures up to 900°C, the inner scale was gray and x-rayed as CoO; the outer scale was grayish black and x-rayed as Co_3O_4. Above 900°C the inner layer was

[3] Wagner (2) gives the composition as $Co_{.994}O$ at 1000°C. However, as Kubaschewski points out (37), the double-layer of CoO found by Preece and Lucas implies that the inner layer possesses vacant anion sites (metal-excess), whereas the outer layer possesses vacant cation sites (metal-deficit).

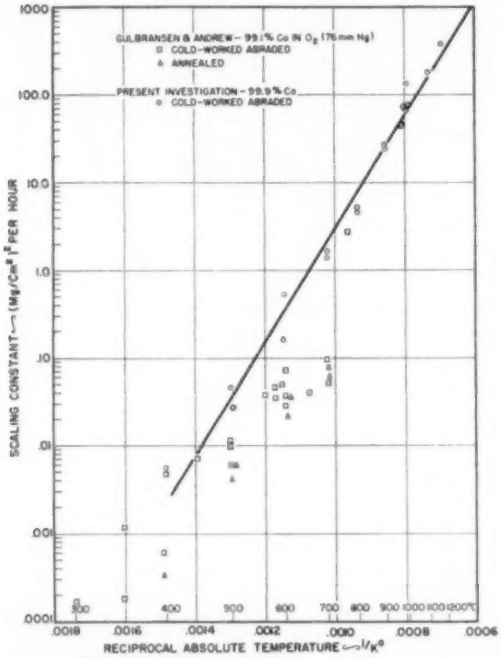
GULBRANSEN & ANDREW – 99.1% Co IN O_2 (76 mm Hg)
□ COLD-WORKED ABRADED
△ ANNEALED
PRESENT INVESTIGATION – 99.9% Co
○ COLD-WORKED ABRADED
SCALING CONSTANT — (Mg/Cm²)² PER HOUR
RECIPROCAL ABSOLUTE TEMPERATURE — 1/K°

FIG. 3. Oxidation of cobalt in air. Scaling constant calculated from parabolic rate law plots in the time interval of 1–2 hr.

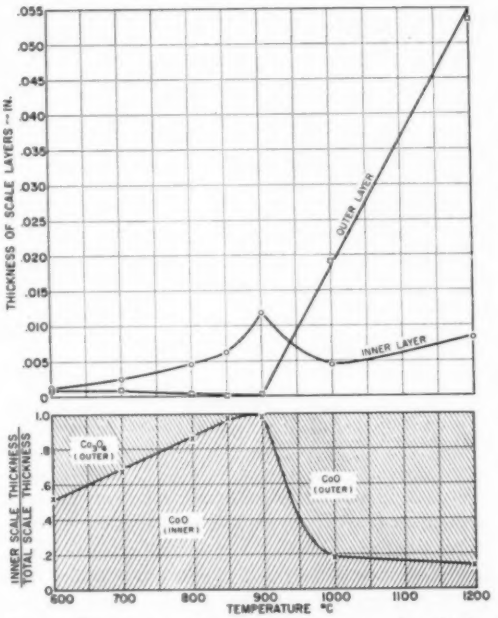

FIG. 4. Effect of scaling temperature on the thickness and composition of the scale layers formed on cobalt heated in air for 100 hr.

a thin brown; the outer layer was a crystalline grayish black, but both x-rayed as CoO.

The outer Co_3O_4 layer occupied about 50% of the total scale thickness at low temperatures (600°C) but became relatively thinner as temperature went up until, at a critical temperature of about 900°C, it disappeared. Of special note is the fact that no break is found in the Arrhenius plot at this temperature. As the temperature was further increased, the outer layer of CoO first appeared as a relatively thin layer but increased gradually until at 1200°C it occupied 90% of the total scale thickness. These relationships are shown in Fig. 4.

Bradley and Jay's method (39) was used to calculate the lattice parameter of the outer and inner CoO layers formed above 900°C. The same diffraction lines of identical intensity were obtained with powder patterns. The extrapolation of lattice parameter to $\cos^2\theta = 0$ ($\theta = 90°$) gave a value of 4.2826Å, which agrees with 4.260Å reported in the literature (16). The NaCl-type structure of CoO was confirmed by comparing theoretical and observed intensities. Good agreement was found except for the high intensity line observed from the (220) plane.

X-ray diffraction patterns of the inner brown and the outer grayish-black CoO layer were also obtained with the spectrogoniometer. This arrangement gives reflections only from those crystallographic planes that are parallel to the specimen surface. The inner brown layer when irradiated *in situ* gave all reflections for CoO, indicating a reasonable degree of randomness. The outer surface of the gray-black scale when irradiated *in situ*, however, gave only one diffraction line, that due to the (200) plane, indicating that virtually all grains had their cubic plane

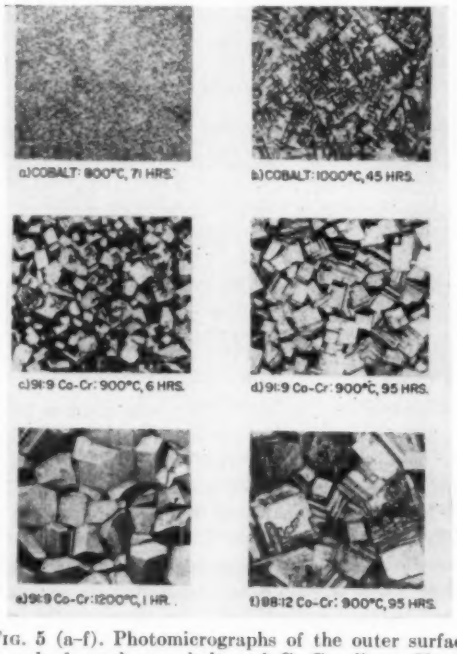

FIG. 5 (a–f). Photomicrographs of the outer surface of the scale formed on cobalt and Co-Cr alloys. Unetched and unpolished. 300× before reduction for publication.

parallel to the scale surface. Further evidence of this crystallographic orientation was found in the photomicrographs of the unetched and unpolished surface of the outer scale, Fig. 5b. The scale surface is covered with growth figures having square or rectangular designs which is compatible with the orientation found by x-rays.

The growth of the oriented scale layer could occur (*a*) by nucleating pseudomorphically on an oriented substrate [examples of which are given by Pfeil (40)], (*b*) by nucleating preferentially on any arbitrary substrate [examples of this are the orientations of zinc cast against air, liquid lead, etc. (41, 42)], or (*c*) by nucleating randomly on any arbitrary substrate but growing preferentially. The first possibility seems unlikely. The lattice parameter of cubic CoO is 4.28Å, while that of cubic cobalt is 3.54Å. This combination of parameters would not produce a match between the metal and the oxide lattice for any pair of planes and directions. Moreover, it is unlikely that the method by which the cobalt was produced would yield a highly oriented structure capable of initiating an oriented substrate pseudomorphically. It should be pointed out that an inner brown layer exists between the metal and oriented scale, although it need not have existed there when the oriented scale was first formed.

The scale formed at 500°–900°, when irradiated *in situ* with the spectrogoniometer, revealed that the outer layer (Co_3O_4) had no texture, while the inner layer (CoO) had grown with the (111) and (220) planes parallel to the growth front, as evidenced by the disproportionately strong reflections from these planes. Microscopic examination of the unetched and unpolished outer surface of the scales formed between 500° and 800° showed the scale to be fine grained, see Fig. 5a.

Since the CoO was found as a double layer above 900°C the growth mechanism was studied by noting the position of the nichrome suspension wire in the scale. For a long enough scaling time and with a thick specimen (0.100 in.) the wire was buried in the scale at or close to the CoO-CoO interface, suggesting that the outer CoO layers grows by diffusion of cobalt ions outward and the inner CoO layer grows by diffusion of oxygen ions inward,[4] as previously noted by Preece and Lucas (1). The square of the thickness of each layer as a function of time at 900° and 1000°C gave a straight line, indicating that the parabolic law of growth is followed for individual layers.

To check the possibility that the scale formed at short times in the range of temperatures from 500° to 800°C differed from that at long times, the metal was oxidized at 500°C for 1 hr. Glancing x-rays of the surface revealed cobalt metal and the three strongest lines of Co_3O_4. This would indicate that at short times the reaction involving Co_3O_4 is rate-determining, whereas at long times the rate-determining reaction involves CoO or both CoO and Co_3O_4. As previously noted, the reaction at short times in the 500°–800°C temperature range proceeds at a higher rate than that at long times. Above 900°C where only CoO is formed, the reaction rate is the same at short and long times. Yet, it is interesting to note that the rate constants calculated for the temperature range from 400° to 1200°C for short times (the time interval of 1–2 hr) can be fitted to a straight line in an Arrhenius plot, Fig. 3, even though the rate-determining reaction presumably involves Co_3O_4 at low temperatures and CoO at high temperatures.

Thus, the interpretation of the break in the curve of log K vs. $1/T$ based on long time intervals, Fig. 2, cannot be explained adequately by a change in scale composition. An explanation cannot be given at the present time.

[4] The growth mechanism at low temperatures could not be determined by this method since the scale formed was too thin.

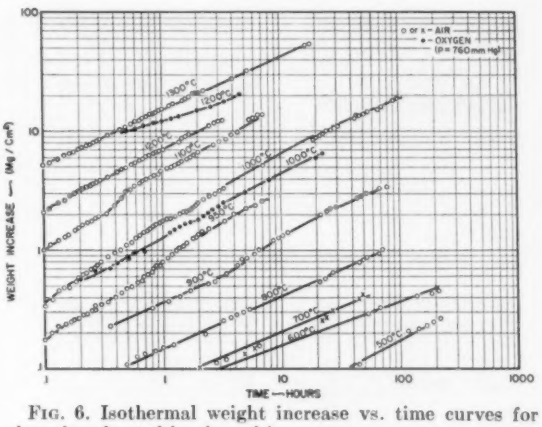

FIG. 6. Isothermal weight increase vs. time curves for chromium heated in air and in oxygen.

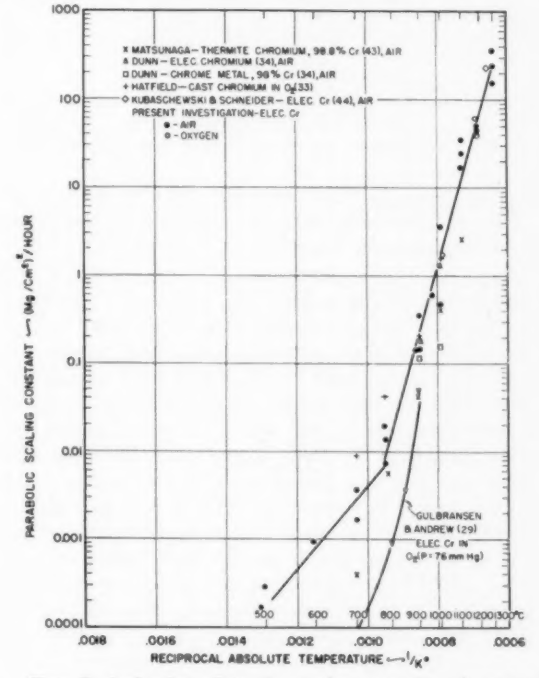
x MATSUNAGA — THERMITE CHROMIUM, 98.8% Cr (43), AIR
Δ DUNN — ELEC. CHROMIUM (34), AIR
□ DUNN — CHROME METAL, 99% Cr (34), AIR
+ HATFIELD — CAST CHROMIUM IN O₂ (33)
◇ KUBASCHEWSKI & SCHNEIDER — ELEC. Cr (44), AIR
PRESENT INVESTIGATION — ELEC. Cr
• - AIR
o - OXYGEN
GULBRANSEN & ANDREW (29)
ELEC. Cr IN O₂ (P = 76 mm Hg)
PARABOLIC SCALING CONSTANT — (Mg / Cm⁴)² / HOUR
RECIPROCAL ABSOLUTE TEMPERATURE — 1/K°

FIG. 7. Arrhenius plot of reaction rate for chromium heated in air and in oxygen.

Scaling Behavior of Chromium

Weight increase measurements as a function of time are plotted on a log-log scale in Fig. 6. The parabolic law of scaling is essentially obeyed (after an initial deviation) between 500° and 1300°C in air and at 1000° and 1200°C in oxygen (P_{O_2} = 760 mm Hg). Chromium scaled at about the same rate in oxygen as in air. The parabolic scaling constants determined from the slopes of the straight lines observed in the plots of weight increase squared against time are plotted on a log scale against the reciprocal of absolute temperature in Fig. 7. The present values are

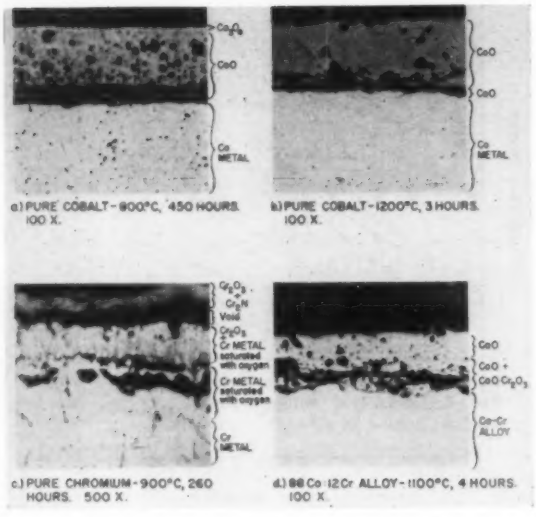
CoO
Co METAL
a) PURE COBALT - 900°C, 450 HOURS. 100 X.
CoO
CoO
Co METAL
b) PURE COBALT - 1200°C, 3 HOURS. 100 X.
Cr METAL saturated with oxygen
Cr METAL
c) PURE CHROMIUM - 900°C, 260 HOURS. 500 X.
CoO
CoO +
Co-Cr ALLOY
d) 88 Co-12 Cr ALLOY - 1100°C, 4 HOURS. 100 X.

FIG. 8 (a–d). Microstructures of scale formed on cobalt, chromium, and Co-Cr alloy. Specimens air cooled after scaling at indicated temperatures and times. Unetched.

in fair agreement with those reported by Hatfield and by Dunn and are higher than those given by Matsunaga and by Gulbransen and Andrew.[5] It is apparent that as in the case of some other metals such as copper (45), iron (46), and possibly cobalt (*see* Fig. 2) there is a break in the curve. At temperatures above 800°C, the slope of the curve is three times as great as that at lower temperatures.

At low temperatures in air (500°–700°C) an adherent green scale, identified as Cr_2O_3 by x-rays, is formed. At high temperatures (800°C and up) in air or in oxygen, the outer surface of the scale is gray-black; however, after scraping the surface, the scale is noticeably green in color.

X-ray diffraction patterns of the black scale formed at 1000°C for 50 hr in air and then water-quenched revealed Cr_2O_3 only. X-ray results on the black scale formed at 900°C in 260 hr in air but then air-cooled to room temperature showed, in addition to the Cr_2O_3 lines, all the lines of β Cr_2N. Although not conclusive, these two tests indicate that the scale forms as Cr_2O_3 with nitrogen dissolved in it, and decomposes on air cooling but not on water quenching to room temperature. The scale formed at 1000° and 1200°C in oxygen consisted of Cr_2O_3 only.

Microscopic examination of specimens scaled in air revealed some interesting features. After high temperature scaling four zones were evident (*see* Fig. 8c). In order, these were: (*a*) the chromium metal matrix extensively cracked; (*b*) a darker, mottled zone indicating oxygen diffusion into the metal; (*c*) a two-phase structure consisting of Cr_2O_3 particles and chromium metal; and (*d*) an

[5] Gulbransen and Andrew also reported lower scaling rates in the case of nickel (56) and cobalt (see Fig. 2). The lower scaling rates of chromium obtained by Matsunaga may be due to the rather impure metal used, since the presence of lower valency impurities would, according to Wagner, lower the oxidation rate of a metal forming a metal-deficit oxide. However, there is disagreement as to whether Cr_2O_3 is a metal-deficit (27) or a metal-excess oxide (28) when formed on chromium.

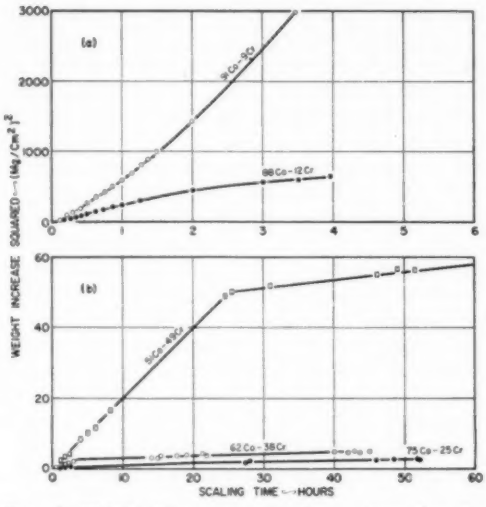

FIG. 9. Weight increase squared vs. time for Co-Cr alloys heated in air at 1100°C.

outer scale consisting of Cr_2O_3 or of Cr_2O_3 and β Cr_2N. These features indicate that chromium oxidizes largely, if not wholly, by the diffusion of oxygen ions inward. These same features were observed after low temperature scaling with the exceptions that the chromium matrix was less extensively cracked, and the presence or absence of the Cr_2O_3-Cr zone could not be determined since the specimens could not be polished without tearing away the outer zone(s).

The break in the Arrhenius curve of log K vs. $1/T$, Fig. 7, might be interpreted in the light of Valensi's theory (45) as being set by one scale product of chromium at low temperatures and another product at high temperatures. It is true that only green Cr_2O_3 is formed at low temperatures and in all probability this portion of the curve is set by the scaling rate of Cr_2O_3 only. The interpretation of the upper portion of the curve presents difficulties, however. At 900°C and up, the black scale formed in air is presumably Cr_2O_3 with (quadrivalent) nitrogen dissolved in it. This could conceivably cause defects in the anionic lattice, thereby increasing the scaling rate by increasing the rate of diffusion of oxygen. Such an explanation has been offered in the case of zirconium (47). However, since the scaling rate of chromium in oxygen was about the same as that in air, it would seem that nitrogen is not necessary for the upper portion of the curve.

Another possibility to account for the break in the Arrhenius curve could be due to the difference in crack density observed in chromium. At low temperatures, the extent of cracking is slight, resulting in a slower penetration of oxygen and a relatively low scaling rate. At high temperatures the metal is extensively cracked, resulting in a faster penetration of oxygen and a higher scaling rate than would be expected from an extrapolation of the low temperature portion of the curve.

Scaling Behavior of Co-Cr Alloys

Each of the alloys scaled at 900°–1200°C showed a deviation from a single parabolic scaling rate, as noted by

TABLE II. *Oxidation rate constants for* Co-Cr *alloys*

Weight % chromium	First parabolic rate	Second parabolic rate	End of first parabolic rate
	900°C		
	$mg^2/cm^4/hr$	$mg^2/cm^4/hr$	*hr*
8.85	22.5, 28.9	—	—
12.25	12.6	—	—
25.57	0.0040, 0.0050	0.0015, 0.0022	60
38.33	0.013, 0.022	0.0030, 0.0021	25
48.50	0.058	0.023	30
	1000°C		
8.85	294	—	
12.25	89	—	
25.57	0.017	0.0055	50
38.33	0.045, 0.073	0.013, 0.020	25
	1100°C		
8.85	445, 581	—	—
12.25	250	—	—
25.57	0.090	0.034	25
38.33	0.25	0.056	5
48.50	2.0	0.22	25
	1200°C		
8.85	860	—	—
12.25	435	—	—
25.57	0.44	0.090	3
38.33	1.2	0.40	2
48.50	3.5	1.4	15

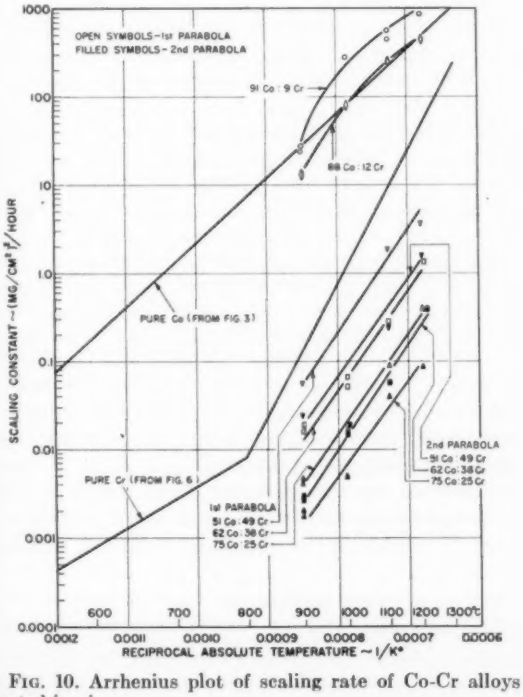
OPEN SYMBOLS–1st PARABOLA
FILLED SYMBOLS–2nd PARABOLA
91 Co : 9 Cr
88 Co : 12 Cr
PURE Co (FROM FIG. 3)
PURE Cr (FROM FIG. 6)
1st PARABOLA
91 Co : 49 Cr
62 Co : 38 Cr
75 Co : 25 Cr
2nd PARABOLA
91 Co : 49 Cr
62 Co : 38 Cr
75 Co : 25 Cr
SCALING CONSTANT ~ (MG/CM²)²/HOUR
RECIPROCAL ABSOLUTE TEMPERATURE ~ 1/K°
600 700 800 900 1000 1100 1200 1300°C
0.0012 0.0011 0.0010 0.0009 0.0008 0.0007 0.0006

FIG. 10. Arrhenius plot of scaling rate of Co-Cr alloys heated in air.

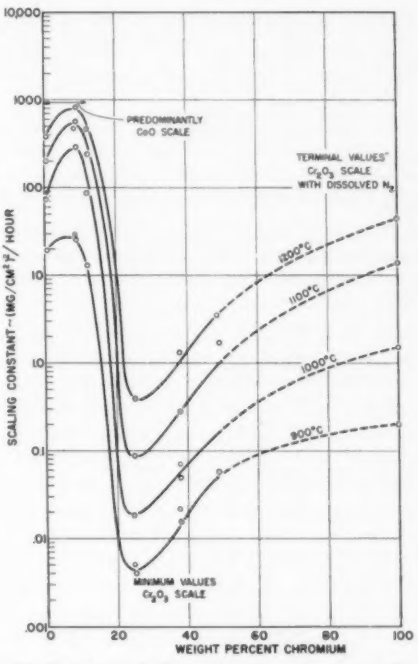

FIG. 11. First parabolic scaling constant vs. alloy composition for Co-Cr alloys heated in air.

a departure from a straight line relationship in plots of weight increased squared vs. time. Examples of these curves are shown in Fig. 9. For long scaling times, the 9 and 12% chromium alloys scaled at a higher and a lower rate, respectively, than that predicted by the parabolic rate law. Those alloys containing 25, 38, and 49% chromium, respectively, exhibited two parabolas, the first one originating from approximately zero time and the second setting in after a certain critical time with a lower slope than the first.

The first and second parabolic scaling constants, Table II, obtained from the slopes of the straight lines[6] are plotted in an Arrhenius plot of the reaction rate (log scale) against the reciprocal of absolute temperature in Fig. 10. It is seen that the data for the 9% and 12% chromium alloys appear to follow a curve, the 9% chromium curve being higher than the 12% chromium. The first and second parabolic scaling constants for 25, 38, and 49% chromium alloys adhere to a single straight line.

The first parabolic scaling rates (log scale) are also plotted as a function of the alloying element (chromium) for constant scaling temperatures in Fig. 11. It is apparent that at a constant temperature the addition of chromium up to about 9% increases the scaling rate three times over that of pure cobalt. Further additions tend to decrease the scaling rate, until at about 25% chromium a pronounced minimum is obtained. Increasing the chromium content thereafter increases the scaling rate, approaching the scaling rate of pure chromium as a limit.

Scale structures as revealed by x-rays are summarized

[6] In the case of the 91:9 and 88:12 Co-Cr alloys where a straight line was not obtained in the plots of w^2 vs. t the scaling constant was taken as the value of the weight increase square after 1 hr.

TABLE III. *Scaling patterns of* Co-Cr *alloys*

Scaling pattern	Inner layer	Outer layer
1	$CoO + CoO \cdot Cr_2O_3$	CoO*
2	(Cr_2O_3 + CoO and/or	$CoO \cdot Cr_2O_3$)†
3	—	Cr_2O_3‡

* Co_3O_4 detected along with CoO at 900°C; only CoO above 900°C.

† Whether or not a multilayered scale was present could not be determined since the scale formed was too thin.

‡ No cobalt was detected in these scales by a Feigl spot test (48).

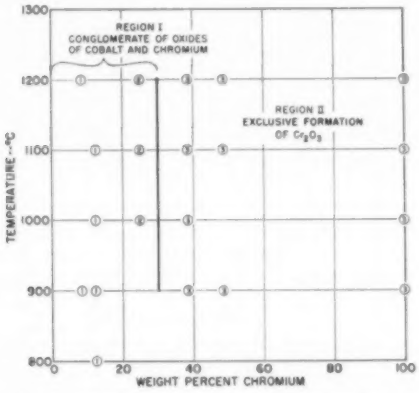

FIG. 12. Composition of scales formed on Co-Cr alloys heated in air. Scaling patterns are given by encircled numbers.

in Table III. Scales were formed on the alloys in one of three different patterns listed in Table III, depending upon alloy composition and temperature as shown in Fig. 12.[7]

A typical microstructure of the scale formed according to Pattern I is given in Fig. 8d. (Microstructures of the scales formed according to the other two patterns could not be obtained since the scales exfoliated on cooling to room temperature.) Glancing x-rays revealed that the surface scale of Pattern I (91:9 and 88:12 Co-Cr alloys) was highly oriented with the (200) plane (d = 2.13) parallel to the surface of the specimen, similar to the case of the outer scale formed on pure cobalt. Photomicrographs of the oriented outer surface are shown in Fig. 5 (e–f).

DISCUSSION

As in the case of Ni-Mn alloys (36), the scaling patterns of Co-Cr alloys can be laid out with a fair degree of certainty in schematic isothermal sections of the ternary Co-Cr-O phase diagram to aid in visualizing the progressive changes in scaling behavior wrought by alloy composition, Fig. 13(a–c).

The dotted paths shown in Fig. 13 were constructed so as to satisfy the demands of the experimentally observed

[7] In some cases the scaling pattern was also dependent upon time at the scaling temperature; however, the patterns plotted in Fig. 10 pertain to the longer scaling times where steady state is assumed to hold. A complete record of the description and x-ray identification of the scales may be obtained from the authors.

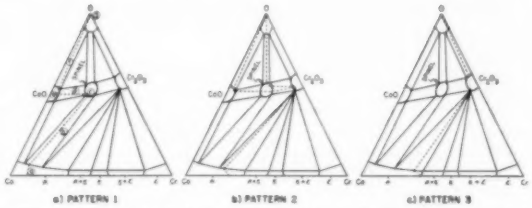

FIG. 13 (a–c). Schematic isothermal sections of the Co-Cr-O equilibrium diagram showing the scaling patterns of Co-Cr alloys.

scale structures. (The path must place the compounds found in the various layers in their proper order; it must reveal a progressive oxygen gradient and still be compatible with the topology of the phase diagram.)

Pattern I.—As Fig. 12 shows, Pattern I is found on relatively cobalt-rich alloys only (91:9 Co-Cr and 88:12 Co-Cr). The path thus starts on the Co-Cr edge of the ternary diagram near the cobalt corner (point *a* in Fig. 13a). The path then must be drawn such that no layer(s) would be found between the metal and the inner scale layer of CoO and spinel since no intermediate layer(s) was observed. This can be accomplished by drawing the path through the α metal-spinel zone along the tie-line *b* (crossing some tie lines in this zone would result in a subscale of spinel in the metal matrix), and through the one-phase spinel region *c* (the fact that this one-phase layer was not found may be due to the thinness of this layer). According to Table III the inner scale consists of CoO and spinel, therefore the path must cross some tie-lines in this two-phase region (point *d*). The outer layer of the scale according to Table III is CoO, hence the path is drawn through this one-phase region to indicate this fact (point *e*). The path then is carried out to the oxygen corner of the diagram (point *g*) along a tie-line between the CoO field and the oxygen field (point *f*) to indicate the sharp interface between the outer layer of CoO and the surrounding air.

Since the inner scale layer formed on the alloys which followed this scaling pattern contained only a small amount of spinel, the total scale can be considered as consisting essentially of a double layer of CoO, similar to the scales formed on pure cobalt at corresponding temperatures. And, as in the case of pure cobalt, this implies that outer scale layer is metal-deficit and grows by outward diffusion of cobalt ions, while the inner scale layer is metal-excess and grows by inward diffusion of oxygen ions. Thus, the sharp interface between the inner and outer scale layers (see Fig. 8d) may mark the original metal surface as noted by Preece and Lucas (1). This means, too, that the spinel in the inner layer was formed by the diffusion of oxygen ions inward; the fact that cobalt oxide is found exclusively in the outer layer also implies that the cobalt ion diffuses outward at a much higher rate than the chromium ion (indeed, if the chromium ion diffuses outward at all).

Pattern 2.—This pattern was followed only by the 75:25 Co-Cr alloy. The path taken by this pattern is not known exactly since the relative location of the component oxides in the scale could not be fixed, i.e., it could not be

determined if a given oxide was located in the inner scale layer or the outer layer or both, because the scale formed was very thin (this alloy had an extremely low scaling rate) and the scale exfoliated completely on cooling to room temperature. However, the path(s) may be deduced from a consideration of the following factors. First, it is known that the scale is predominately Cr_2O_3 with some CoO and/or spinel. Second, it is assumed that any CoO is to be found in the outer portions of the scale since the cobalt ion diffuses faster than the chromium ion. When all three of the oxides listed in Table III are to be found in the scale, the path may follow the lower route shown in Fig. 13b. When only Cr_2O_3 and spinel are to be found, then the path may follow the upper route shown in Fig. 13b.

It is to be noted that the 75:25 Co-Cr alloy effects a tremendous decrease in the scaling rate and that the first parabolic function corresponds to a scaling pattern which results in a scale consisting predominately of Cr_2O_3 with some spinel. Thus, it is apparent that Cr_2O_3 is responsible for the enormous drop in the scaling rate, not the spinel oxide.[8]

The second parabolic function for this alloy shows a still greater resistance to scaling, yet the scale may contain some CoO in addition to Cr_2O_3 and spinel which makes it difficult to ascribe the change in scaling rate to a change in scale composition since the formation of CoO indicates relatively poor scaling resistance. However, it is apparent that, in a scale consisting mainly of Cr_2O_3, this oxide acts as an extremely effective barrier to the diffusion of oxygen ions inward or to a diffusion of metal ions outward.

Pattern 3.—Since this scaling pattern corresponds to the formation of Cr_2O_3 exclusively,[9] the only possible path is that given in Fig. 13c. The 62:38 and the 51:49 Co-Cr alloys which scaled according to this pattern exhibited two different parabolic scaling rates during the course of oxidation at a given temperature, yet the scale x-rayed as Cr_2O_3 for either the first or second parabola even though the second parabolic rate is about ten times less than the first parabolic rate. As in the case of the 75:25 Co-Cr alloy, this change in scaling rate cannot then be ascribed to a change in scale composition.

In general, all patterns in Fig. 13 have a similar shape; instead of being straight lines from the original alloy composition to the oxygen corner of the diagram, they veer first to the chromium-rich side of a direct route and then to the cobalt-rich side. As pointed out previously, this implies that the cobalt ion diffuses outward at a much higher rate than the chromium ion. However, when the chromium content of the original alloy is high, Cr_2O_3 is formed exclusively and the change in direction of the path to the cobalt-rich side is not obtained. The minimum chromium content of the original alloy necessary for exclusive formation of Cr_2O_3 is drawn in as a solid line in Fig. 12.

The increase in the scaling rate by small additions of chromium to cobalt has also been found with small additions of chromium to nickel (50). This increase has been explained on the basis that trivalent chromium dissolves in the metal-deficit CoO (or NiO) and replaces some of the divalent cobalt (or nickel) ions (51), thus providing new cation defects for the diffusion of cobalt (or nickel) ions.[10]

Conversely, the argument that cobalt additions to chromium effect a decrease in the scaling rate on the basis of a decrease in the number of vacant cation sites may hold in the present case and account for the excellent scaling resistance at about 25% chromium. This would, however, require that Cr_2O_3 be a metal-deficit oxide, which does not seem likely since Cr_2O_3 is formed by the diffusion of oxygen ions inward, at least in the case of pure chromium.

An alternate possibility to account for the drop in scaling rate brought about by cobalt additions to chromium is analogous to the simple case of Ni-Pt alloys investigated by Kubaschewski and Goldbeck (51). They analyzed their results on the basis of diffusion and activity considerations put forth by Wagner (50) and, although their interpretation has been disputed (52), their data show clearly that oxidation rate decreases with increasing platinum content and that NiO is formed exclusively. Similarly, Cu-Pt alloys (52) show a decrease in the oxidation rate with increasing platinum, although copper oxide is formed exclusively. The Co-Cr alloys showed that in the range of chromium contents from 100 to 25% cobalt acts noble with respect to chromium, i.e., only chromium oxidizes. The attendant decrease in scaling rate as the chromium content decreases could be reconciled as due to the same effect as in the Ni-Pt and Cu-Pt alloys, dilution of the base metal (chromium) in the alloy, leading to a decrease in the scaling rate.

Last, it is to be noted that, although the Co-Cr alloys containing more than about 20% chromium exhibit high scaling resistance in continuous oxidation runs, the scales formed on these alloys spalled badly on cooling to room temperature. This would seem to preclude their use in cyclic heating and cooling service unless the spalling resistance could be improved, as in the case of Ni-Cr alloys (55), by the addition of small quantities of such elements as silicon which "peg-in" the external scale.

Conclusions

1. At a given temperature the scaling rate of Co-Cr alloys first increased with low chromium additions, then dropped precipitously with further chromium additions reaching a minimum at about 25% chromium. Higher chromium contents effected a rise in the scaling rate reaching the scaling rate of pure chromium as the upper limit.

2. The composition of the scale formed on Co-Cr alloys was dependent upon alloy composition. Above a critical

[8] Recent work at this laboratory indicates that the exclusive formation of Cr_2O_3 is responsible for the excellent scaling resistance of iron-base and nickel-base alloys containing about 25% chromium. In fact, the scaling rate at this critical concentration of chromium is independent of the base metal, be it cobalt, nickel, or iron.

[9] A number of analyses have been proposed for predicting the minimum concentration of an alloy constituent necessary for the exclusive formation of its oxide (2, 49), but none of these applies here since they are based on assumptions that are not met in the present case.

[10] The deleterious influence due to lattice defects may overshadow any beneficial effect due to the small amounts of spinel and/or Cr_2O_3 found in these alloys.

concentration of about 25% chromium (Region II), the scale consisted exclusively of chromium oxide; below this critical concentration (Region I) complex scales of the oxides of both cobalt and chromium were formed.

3. In Region I the scales were such that the cobalt ion must diffuse outward faster than the chromium ion.

4. Spinel formation observed in the complex scales had no apparent beneficial effect on the scaling resistance.

5. The poor spalling resistance of the Co-Cr alloys would seem to preclude their use as oxidation resistant components in cyclic service operation.

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Hydrogen Evolution from Dissolving Titanium-Oxygen Alloys in Hydrofluoric Acid and the Constitution of Ti-O Alloys

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ABSTRACT

Titanium-oxygen alloys dissolve in HF according to the reaction $TiO_x + 3HF \rightleftharpoons TiF_3 + xH_2O + 0.5\,(3 - 2x)H_2$, with a maximum for $x = 1.5$, which means that Ti_2O_3 dissolves without hydrogen evolution. Higher titanium oxides do not dissolve in HF. The determination of the end point of the above reaction was affected by a secondary, but very slow reaction $TiF_3 + HF \rightleftharpoons TiF_4 + 0.5H_2$. Nevertheless, the experimental results agreed within ±2% for the first reaction for titanium containing oxygen up to 33 at.%. Titanium-oxygen alloys do not represent titanium oxygen solid solutions but solid solutions of titanium oxides and titanium metal.

HF dissolves titanium readily according to the equation (1, 2):

$$Ti + 3HF \rightleftharpoons TiF_3 + 1.5H_2 \qquad (I)$$

Also, Ti-O alloys (3) dissolve in HF with hydrogen gas evolution. However, it was not known how the oxygen in the metal would change the amount of hydrogen evolved and how it would influence the valency of the titanium ions produced. It was also thought that the study of the behavior of the alloys in HF might reveal some further clues concerning the structure of these alloys, which is still uncertain (4, 5).

Dissolution of Ti-O alloys TiO_x may occur in a manner similar to the dissolution of other soluble oxides according to the reaction:

$$TiO_x + 3HF \rightleftharpoons TiF_3 + xH_2O + 0.5(3 - 2x)H_2 \qquad (II)$$

By measuring the amount of hydrogen developed and knowing the composition of the Ti-O alloys, the correctness of equation (II) was checked.

Preparation and Analysis of Ti-O Alloys

The alloys were prepared by heating titanium powder (+65 mesh, 99.7% pure),[1] with a calculated amount of TiO_2 (99.9% pure);[2] the dry materials were weighed, mixed, and put into alundum or zirconia crucibles (in case of oxygen content over 25% by weight) and heated in vacuum resistance furnace for 4 hr at 1100° or 1400°C, respectively. Samples of high oxygen content were crushed and reheated at 1400°C for 2–4 hr to secure uniform composition. The charges, usually sintered in one solid piece, were crushed, ground, and stored in a desiccator. The color of the alloys No. 2 to 6 (Table I) was light gray, resembling pure titanium powder. The brittleness of the substance increased with increasing oxygen content. The color of alloy 7 and 8 was darker. Alloy 10 had a greenish tint, while alloy 11 was nearly black. Under the microscope the latter displayed crystalline grains of a dark violet color. The ten alloys prepared, varying in oxygen content from 3 to 60 at. %, were analyzed for their titanium content, and it was assumed that the balance was oxygen. No direct oxygen determinations were made.

Analyses were performed according to a method described by Rahm (6), but slightly modified. It consists in titrating the dissolved titanium alloy with ~N/10 aqueous solution of $FeNH_4(SO_4)_2$, standardized against pure TiO_2. Approximately 200–300 mg of each alloy was dissolved in 10 ml concentrated H_2SO_4 containing 5 g anhydrous sodium sulfate, and the titanium of the obtained solutions was reduced to the trivalent state by aluminum for titration under CO_2. Reagent grade chemicals were used in every instance.

Experimental Procedure

Samples of the alloys of the compositions as given in Table I were dissolved in HF in a special apparatus and the hydrogen evolved was collected. First, the finely ground charge of the alloy was weighed in a small platinum crucible, which was placed on a glass or polyethylene spoon cemented to a Pyrex glass joint. The whole was then introduced into a 200 cm^3 Erlenmeyer flask as previously described (7). The stopper of the flask was equipped with two capillaries, one of which was so arranged that the air in the flask could be displaced through it, before the dissolution procedure, by pure hydrogen, in order to prevent the oxidation of the trivalent titanium ions formed later (1). The second capillary served to lead the evolved hydrogen into the gas measuring buret. The flask, the inside of which was lined with paraffin wax, was submerged in a constant temperature water bath (25 ± .05°C). Wherever possible, glass joints were used in order to minimize loss of hydrogen by diffusion through rubber connections. After flushing the apparatus with hydrogen for some time, and after thermal equilibrium had been reached, the valves were closed, and the spoon sealed to the glass joint

[1] Supplied by the Belmont Smelting and Refining Works, Inc.

[2] Fisher Scientific Co.

TABLE I. *Hydrogen volumes (reduced to normal conditions) as developed by various* TiO_x *alloys in* HF

Concentration of HF: 3*N* (30 ml) for alloys No. 1–8, and 6*N* (60 ml) for No. 9–11

Alloy No.	Ti by chem. anal.		x from chem. anal. in g atoms	H_2 in ml/g alloy		Δ in	
	Wt.%	At.%		Observ.	Calc. eq(II)	ml	%
0	100.0	100.0	0	—	702	—	—
1	99.9*	99.9*	<0.001	697	700	−3	−0.43
2	98.7	96.3	0.038	677	675	+2	+0.29
3	98.3	95.1	0.052	666	666	±0	±0.00
4	97.0	91.5	0.093	646	639	+7	+1.1
5	96.7	90.7	0.103	619	632	−13	−2.0
6	94.7	85.6	0.168	580	590	−10	−1.7
7	92.7	80.9	0.236	542	548	−6	−1.1
8	86.0	67.2	0.488	410	407	+3	+0.73
9	76.4	52.0	0.925	225	206	+19	+8.4
10	74.5	49.4	1.024	185	166	+19	+10.0
11	66.1	39.4	1.538	5.6	0	+5.6	—

* Obtained by dissolving Ti produced by thermal decomposition of titanium iodide. The balance in all alloys is oxygen.

was overturned so that the crucible with the charge dropped into the acid. Usually the alloys were completely dissolved in 20 min.

Results

Although the method of working and collecting the hydrogen evolved seemed to be very simple, complications arose because the solution continued to evolve hydrogen after the titanium alloy was completely dissolved. In analogy to the reaction of divalent titanium ion with hydrogen ion (acids) (8):

$$Ti^{2+} + H^+ \Rightarrow Ti^{3+} + 0.5H_2 \qquad (III)$$

or of gaseous hydrogen fluoride with titanium fluoride (at 600°C) (9):

$$2TiF_3 + 2HF \Rightarrow 2TiF_4 + H_2 \qquad (IV)$$

it was assumed that a reaction simliar to (IV) could also occur in aqueous solutions, as HF was used in excess and TiF_3 always was formed during the dissolution processes. The presence of TiF_3 was indicated by the greenish color of the resulting acidic solutions, and by the instantaneous decoloration of large amounts of $KMnO_4$ solutions if added to them. In fact the possibility of a reaction like equation (IV) in aqueous solutions was subsequently proved by special experiments: (*a*) after the dissolution was completed, the greenish color of the solution gradually faded out; (*b*) the amounts of $KMnO_4$ solutions necessary to oxidize the solution gradually decreased; and (*c*) simultaneously the rate of hydrogen evolution dropped. However, ions of trivalent titanium were present even then, when the rate of hydrogen evolution according to equation (IV) after 20 and more hours of reaction approached zero. The slow rate of this reaction agrees with the small normal potential $E_0 = -0.05$ volts for $Ti^{3+} \rightarrow Ti^{4+} + e$ in H_2SO_4 (8). The instability of solutions of trivalent titanium is also known from the literature. For example, it was observed that $TiCl_3$ solutions slowly oxidized even in a

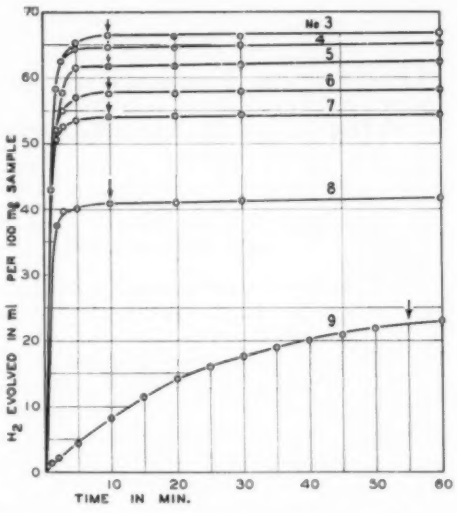

FIG. 1. Amount of hydrogen in ml developed by 100 mg of a TiO_x alloy at a time shown on the abscissa. Arrows indicate the end of reaction (II), numbers—the alloys of Table I.

hydrogen atmosphere; the rate of oxidation was much faster in presence of oxygen (10). As the presence of this gas was completely excluded in these experiments, the only possibility of explaining the oxidation of TiF_3 and hydrogen evolution after dissolution was reaction (IV) or a similar one. The reaction was catalyzed by paraffin, because glass coated with this substance and immersed into the TiF_3-HF solution quickly was covered with growing gas bubbles. Platinum was less effective. Although TiF_3 solutions are unstable, the pure and dry salt exhibits a remarkable stability (9).

Fortunately the rate of reaction (IV) was so slow that it could be completely disregarded in the case of alloys with a low oxygen content as in the beginning of the dissolution reaction (II) the TiF_3 concentration in the solution is low. It was somewhat more difficult to estimate the end of the reaction when large amounts of oxygen were present in the titanium alloy, as the concentration of TiF_3 strongly increased at the start because of rapid dissolution of Ti_2O_3 present in the alloy without any hydrogen evolution [reaction (II), $x = 1.5$]:

$$Ti_2O_3 + 6HF \Rightarrow 2TiF_3 + 3H_2O \qquad (V)$$

So in this case the decreasing rate of the hydrogen evolution reaction (II) was overlapped by an increasing rate due to reaction (IV), thus diminishing the sharpness of the bend of the volume vs. time curve (Fig. 1) and making the estimation of the end of reaction (II) more difficult. The rate of the reaction (IV) declined, as soon as the alloy was dissolved in the acid.

Powdered alloys with a low oxygen content (No. 1 to 8) dissolved completely in 3*N* HF in 10 min, while it took about 1 hr to dissolve the alloy with high oxygen content in the acid twice as strong (alloy No. 9, Fig. 1). After this hour the rate slowed down considerably, indicating that reaction (IV) alone continued. Solutions were slightly

turbid probably because of the presence of TiO_2 which does not dissolve in HF.

How good such an estimation of the end of reaction (II) was is shown in Table I, where the hydrogen volume developed is compared with the volume calculated from equation (II).

Discussion and Conclusions

The fairly good agreement between the observed and calculated hydrogen volumes (Table I) indicates that equation (II) describing the reaction of dissolution of Ti-O alloys in HF is correct. However, in such a case it should be expected that at about $x = 1.5$ (alloy Ti_2O_3) hydrogen evolution by the alloy should be zero. The observed small volume of 5.6 ml is explained by insufficient homogenization of the alloys high in oxygen content, although temperatures up to 1400°C and repeated heating up to 4 hr was used. The proof is that alloys heated at lower temperatures developed larger amounts of hydrogen, meaning that more free titanium which did not react with TiO_2 was left over. Thus the oxide which dissolves in HF without any hydrogen evolution is Ti_2O_3, and the maximum for x in equation (II) is 1.5. If x is larger, no hydrogen is evolved by such alloys.

From the behavior of TiO_x alloys toward HF one clear statement can be drawn, i.e., oxygen is bound chemically by titanium ions with formation of solid solutions of which those with highest oxygen content are represented by Ti_2O_3. Oxides with still larger oxygen content are out of this series, because they do not dissolve in HF. Evidently, at high temperatures oxygen (5) in the form of negative ions diffuses into titanium, migrating in the interstitial space from one titanium positive ion to another. However, dissolution experiments cannot determine what kind of lower oxides are formed inside the titanium metal, because the titanium ions of lower than 3 valency, as soon as they have left the lattice, react with water or with acid according to equation (III) with evolution of hydrogen. So one obtains from the total reaction the impression that all TiO_x alloys consist of a solid solution of metallic titanium which evolves hydrogen in HF and of Ti_2O_3, which does not. Although this behavior is correctly described by reaction (II), there are, on the other hand, experimental facts which contradict this statement and seem to confirm the existence of TiO as a chemical compound (11) and not as a solution $Ti(Ti_2O_3)$. For instance it was found that titanium oxide dissolving in acids produces the ions Ti^{2+} and Ti^{3+} (10); the appearance of the latter is easily explained by reaction (III) or by the dissolution of $Ti(Ti_2O_3)$. The formation of divalent titanium ions could indicate the presence of TiO in the titanium, but the ion Ti^{3+} may also result from the dissolution of the metallic part of $Ti(Ti_2O_3)$ in the acid. Because of this uncertainty it is not possible to say exactly what other oxides besides Ti_2O_3 are present in TiO_x alloys. The phase relationship of the different titanium oxides is described by Bumps, Kessler, and Hansen (12, 13).

Equation (II) can be used for an easy and fast determination of free titanium (as if unbound) or of oxygen (by difference) in titanium oxygen alloys.

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Anodic Coprecipitation of Trace Amounts of Manganese and Silver with Lead Dioxide

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ABSTRACT

The applicability of anodic coprecipitation to the separation of trace amounts of ions from solution has been demonstrated by the carrying of silver and manganese on anodically formed lead dioxide. Neither of these elements could be anodically deposited under the conditions of these experiments in the absence of the lead.

Control of the anode potential is an important factor in the codeposition of an element which, like manganese, can be oxidized to higher valence states which are less readily coprecipitated than is manganese(IV). Likewise, for coprecipitation of silver, the anode potential must be positive enough for the silver(I) to silver(II) oxidation to occur.

Up to the present time, analytical applications of electrodeposition have been concerned almost entirely with the cathode. With the exception of lead and manganese which are precipitated as dioxides, little attention has been devoted to the anode despite the possibility of separating a number of elements. A disadvantage that one can anticipate arises from the fact that a compound rather than an element is formed. As a result, consideration of the solubility of the deposit becomes important, particularly when dealing with trace amounts.

Coprecipitation is frequently used to effect complete deposition at the trace level and there is no reason to expect that electrolytic coprecipitation should be any less effective. Compared to ordinary coprecipitation, the variety of compounds that can be used as a carrier in electrolytic coprecipitation is somewhat limited. However, the possibility of increasing the selectivity by control of the anode potential is a promising compensating factor. The only reported attempt to employ electrolytic coprecipitation for traces involved the carrying of plutonium dioxide with manganese dioxide and was far from successful (1). However, it appears that failure to control the anode potential undoubtedly resulted in oxidation of the plutonium beyond the tetravalent state, thereby forming the less readily coprecipitated plutonyl ion. Likewise, a high anode potential would favor oxidation of manganese beyond the tetravalent state and would mitigate against coprecipitation.

The present paper reports exploratory experiments which demonstrate that trace amounts of manganese and of silver can be quantitatively (and selectively) coprecipitated during the anodic deposition of lead dioxide. Most of the effort was devoted to manganese, silver having been studied only briefly in a qualitative manner to test the expected generality of the conclusions regarding coprecipitation.

Manganese was selected for study because of the favorable radiochemical characteristics of the nuclide, manganese-52, and because of the interesting electrochemical behavior that results from the several oxidation states of manganese in solution. The choice of silver-111 was the result of its being on hand for concurrent use in another study. The choice of lead as the carrying element was largely a matter of convenience. Its deposition behavior was well known and its concentration could be determined rapidly using the polarograph.

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Experimental

Reagents and solutions.—Solutions of carrier-free manganese-52 were prepared by distillation of permanganic acid from solutions of deuteron-bombarded chromic oxide (2). Experiments with similar solutions in the anodic deposition of manganese dioxide had indicated that these solutions were less than 10^{-7}M in manganese. All solutions of manganese except the carrier-free tracer were made up by dilution of a 0.0097M solution of Mallinckrodt reagent-grade manganous nitrate standardized by the bismuthate method (3). All lead solutions were made by dilution of a 0.0988M solution of Mallinckrodt reagent-grade lead nitrate standardized gravimetrically by the lead sulfate method (4). Distilled water was used throughout.

Apparatus.—The potential on the anode was controlled in every case to at least ±3 mv using potentiostats designed by Lamphere (5). The potential was adjusted at the beginning of the run and checked several times during each run using a Rubicon potentiometer reading to ±0.1 mv. Electrolyses were usually carried out in open 250 ml beakers using a volume of 160 ml and platinum gauze anodes of about 13 cm² or 39 cm² in area. Both the platinum wire cathode and the saturated calomel reference electrode (SCE) were connected to the electrolytic solution through suitable agar salt bridges. The cathode solution was 0.5*N* in potassium nitrate. The entire electrolytic set-up including a stirring motor was placed in a box-like plastic hood to protect the solutions from contamination with dust. All *p*H measurements were made with a Beckman Model G *p*H meter.

Procedures.—All solutions of manganese were preelectrolyzed for at least 12 hr prior to the addition of lead to insure that all of the manganese that could precipitate

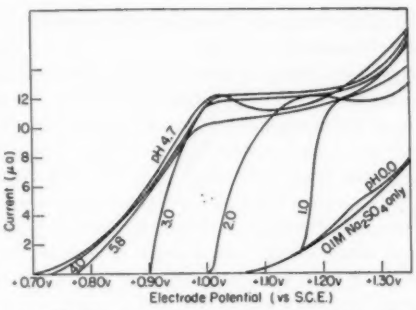

FIG. 1. Effect of *p*H on the polarographic oxidation of 10^{-3} M manganous ion to manganese dioxide at a stationary platinum microelectrode.

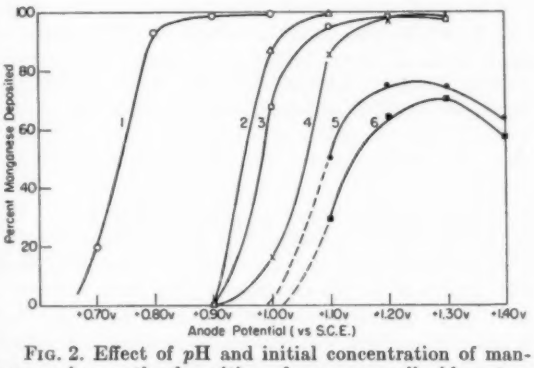

FIG. 2. Effect of *p*H and initial concentration of manganous ion on the deposition of manganese dioxide onto a 10 cm² platinum gauze electrode from 150 ml of 0.5M KNO_3 with an internal cathode.

	1. ○	2. △	3. □	4. ×	5. ●	6. ■
(Mn^{++})	10^{-2}M	10^{-3}M	7×10^{-4}M	3×10^{-4}M	3×10^{-5}M	2×10^{-5}M
Initial *p*H	4.69	3.04	2.53	2.82	2.89	2.89
Final *p*H	6.38	3.39	2.45	2.73	2.79	2.76

by itself would do so. An electrolysis was usually carried out at a particular potential for at least 3 hr or until a constant counting rate indicated that equilibrium had been reached. Duplicate aliquots were withdrawn using 1.00 ml pipets, transferred to lacquer-coated aluminum of copper cups, and counted according to the method or Freedman and Hume (6) using an end-window Geiger-Mueller tube. Ordinarily, 2000 to 5000 counts were obtained on each sample within 2 hr of the sampling time. The range of the duplicates was less than 5% of the total count in every case.

After analysis of the solution, the potential was changed about 0.1 v more positive and the electrolytic procedure repeated. Because of the large volume of solution that was electrolyzed, the portions taken for counting could usually be neglected during the early part of a given run. Toward the end of a run when the accumulated volume of the aliquots became appreciable, a suitable correction was made in calculating the amount deposited.

In the studies of the rates of deposition of manganese and of lead, a polarographic determination of the lead remaining in the solution was made on a 0.50 ml aliquot using the conventional dropping mercury electrode and a Sargent Model XII polarograph. All analyses were made within 3 min of sampling to minimize evaporation. Preliminary standardization of seven lead samples ranging from 10^{-4}M to 10^{-2}M showed a coefficient of variation of ±2.7%.

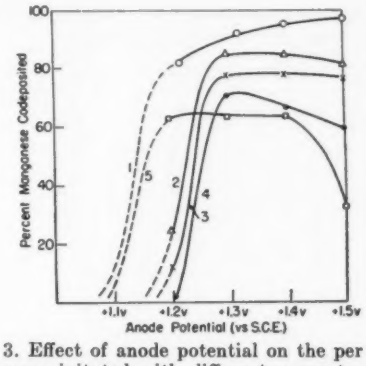

FIG. 3. Effect of anode potential on the per cent manganese coprecipitated with different amounts of lead dioxide onto a 13 cm² platinum gauze anode from 150 ml of 0.5M KNO_3.

	1. ○	2. △	3. ×	4. ●	5. □
mg Pb	200	80	40	20	10
Initial *p*H	2.80	2.82	2.82	2.85	2.89
Final *p*H	2.20 (internal cathode)	1.90	1.98	2.05	2.40

RESULTS

Anodic polarography of manganese.—Before starting the studies of codeposition, preliminary polarographic studies were made on solutions containing millimolar manganous nitrate in 0.1M sodium sulfate and H_2SO_4 in order to find the best conditions to use for the electrolysis. A Sargent Model XXI polarograph with a stationary platinum electrode was employed. Strictly speaking, results cannot be compared with deposition data obtained later on nitrate solutions but, since the two sets of data were consistent, it appeared unnecessary to repeat the polarograms.

Fig. 1 shows that the *p*H range from 1–3 is most suitable for an electrolytic study. Within that range the $E_{\frac{1}{2}}$'s are separated by about 120 mv/*p*H unit which is the shift with the fourth power of the hydrogen ion concentration predicted by the theoretical equation

$$Mn^{+2} + 2H_2O = MnO_2 + 4H^+ + 2e^-$$

At *p*H 2, changing the concentration of manganese to 10^{-4}M and 10^{-5}M produced successive shifts of +0.03 v also in agreement with predictions based upon the same equation. However, the formal potential was about 0.20 v more positive than the value predicted from the standard potential (7).

Effect of anode potential and p*H on deposition.*—As shown in Fig. 2, manganese in concentrations greater than 3×10^{-6}M could be deposited quantitatively in the absence of a carrier at a *p*H above 2.5. More important, however, is the decrease in recovery obtained at +1.40 v, presumably because of oxidation beyond the tetravalent state.

The effect of anode potential on the codeposition of manganese with different amounts of lead dioxide is shown by Fig. 3. Each of these solutions, which contained only tracer manganese of unknown concentration, had been

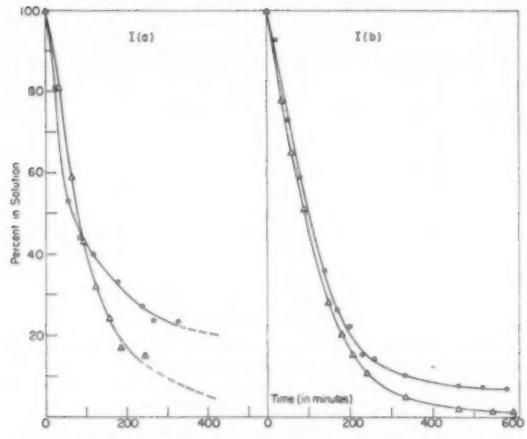

FIG. 4*a*. Rates of coprecipitation of manganese dioxide and simultaneous precipitation of lead dioxide onto a 39 cm² platinum gauze electrode from 160 ml of 0.5M KNO_3 at *p*H 1.0. Anode potential (vs. S.C.E.) 1.372 v; initial concentration, △, lead, I (a), 8.9×10^{-4}M, I (b), 2.52×10^{-3}M; ○, manganese, I (a), 4.8×10^{-8}M, I (b), 1.3×10^{-7}M.

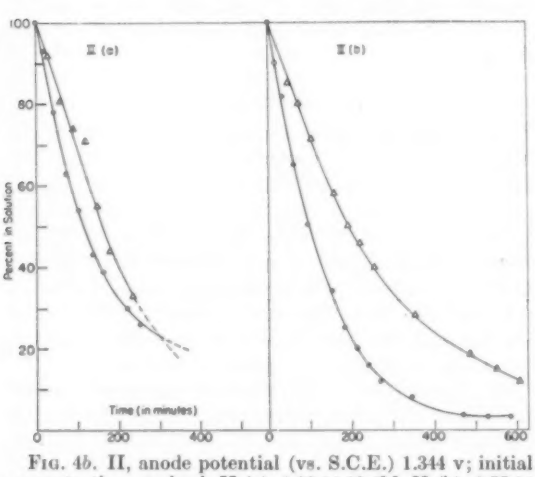

FIG. 4*b*. II, anode potential (vs. S.C.E.) 1.344 v; initial concentration, △, lead, II (a), 1.00×10^{-3}M, II (b), 2.75×10^{-3}M; ○, manganese, II (a), 3.0×10^{-7}M, II (b), 3.5×10^{-7}M.

electrolyzed for 12 hr at an anode potential of +1.20 v to insure that the manganese would not deposit on the platinum gauze anode in the absence of lead. After addition of the indicated amount of lead, electrolysis was allowed to proceed at each potential setting for 3 hr before measurement.

A decrease in *p*H during these electrolyses took place in accordance with the electrode reaction for the formation of lead dioxide.

$$Pb^{+2} + 2H_2O = PbO_2 + 4H^+ + 2e^-$$

In the only run, curve 1, where an internal platinum cathode was used, the final *p*H was out of line with the trend of a lower *p*H for a higher concentration of lead that was observed for the runs in which an external cathode was used. This anomalous behavior was probably due to cathodic evolution of hydrogen.

The downward trend of some of these curves at potentials greater than +1.4 v is again presumed to be due to oxidation of the manganese(II) to a valence higher than four. This was substantiated by the failure of manganese to coprecipitate when a potential of +1.5 v or greater was applied to an anode on which no previous precipitation had taken place. Decrease in deposition at high potentials was not so evident when the amount of lead carrier was increased, but this was probably due to burial of the manganese(IV) atoms within the lead dioxide lattice. The anomalous displacement of the 10 mg lead curve toward less positive potentials is probably due to the higher *p*H of that solution.

It is apparent from these curves that in the *p*H range from 2.7 to 3.0, the optimum anode potential for coprecipitation of manganese is between +1.3 v and +1.4 v (vs. S.C.E.). The upper limit of the anode potential should be dependent upon *p*H and concentration of manganous ion while the lower limit should be dependent not only upon these two factors but upon the concentration of lead ion as well.

Effects of initial lead and manganese concentrations.—To examine the effects of changes in lead and manganese concentrations on coprecipitation, a series of experiments was performed in which the electrolyses took place at a constant anode potential and continued until essentially all of the lead had been precipitated. Four different electrolytic cells (I–IV) were used and two runs (a, b) were made on each. During the course of each electrolysis, lead and manganese concentrations were determined frequently by polarographic and radiochemical methods, respectively. Manganese and lead concentrations were then plotted as functions of time in order to illustrate relative rates of deposition of the two components. Results are shown in Fig. 4.

Because of the high ratio of the initial lead-to-manganese concentrations used in these experiments, it appears safe to assume that the amount of manganese on the surface of the electrode deposit at any time is so small that the electrode has an activity essentially the same as an electrode of pure lead dioxide. Hence, at any given time during the electrolysis, the electrode must appear to the solution almost exactly the same as it did after the first few layers of lead dioxide had precipitated. If this assumption is true, one can select any point on the rate curve for lead, find the point on the rate curve for manganese for the same time, and use these concentrations of lead and manganese as initial values. Any one of such initial concentrations can be used to determine the fraction of manganese coprecipitated at the conclusion of the electrolysis. This procedure was used in three instances (Ib, IIa, IIIa) to evaluate the effect of different initial concentrations of lead on the fraction of manganese codeposited, starting with the same initial concentration of manganese.

For example, to compare runs Ia and Ib at the same initial manganese concentration one would select the time at which the manganese concentration in Ib equalled 4.8×10^{-8} M. This corresponds to 37% (0.48/1.3) of the

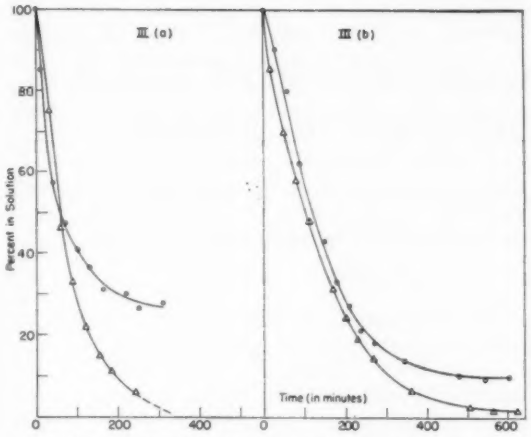

FIG. 4c. III, anode potential (vs. S.C.E.) 1.396 v; initial concentration, △, lead, III (a), 8.5×10^{-4}M, III (b), 3.10×10^{-3}M; ○, manganese, III (a), 4.5×10^{-8}M, III (b), 3.5×10^{-8}M.

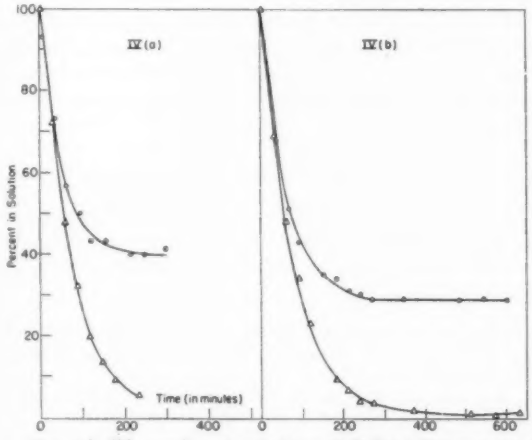

FIG. 4d. IV, anode potential (vs. S.C.E.) 1.376 v; initial concentration, △, lead, IV (a), 7.7×10^{-4}M, IV (b), 2.31×10^{-3}M; ○, manganese, IV (a), 1.4 ml tracer; IV (b), 4.3 ml tracer.

original manganese concentration of 1.3×10^{-7}M. At this same time, the lead concentration is seen to be 34% of the original 2.52×10^{-3}M and is therefore equal to 8.6×10^{-4}M. Using this time as a starting point, the fraction of manganese coprecipitated is the difference between 37% in solution at this starting point and 6.5% at the end of the electrolysis divided by 37% (37-6.5/37 = 0.82).

Table I illustrates the effect of initial concentration of lead at four different manganese concentrations and Table II illustrates the effect of initial concentration of manganese at two different lead concentrations. One can see positive correlation between the fraction of manganese coprecipitated and the initial concentration of lead. However, the effect of changes in the initial concentration of manganese is not clear from these data. In cells I, II, and III, increases of five to eightfold in initial concentration of manganese appeared to have little effect, but in cell IV,

TABLE I. *Effect of initial concentration of lead on the fraction of manganese codeposited*

Cell	Run	Initial concentration, M		Fraction of manganese codeposited
		Lead	Manganese	
IV	b	2.31×10^{-4}	1.4 ml tracer*	0.11
IV	a	7.7×10^{-4}	1.4 ml tracer*	0.60
I	b	8.6×10^{-4}	4.8×10^{-8}	0.82
I	a	8.9×10^{-4}	4.8×10^{-8}	0.77
III	a	7.2×10^{-4}	3.5×10^{-8}	0.65
III	b	3.10×10^{-3}	3.5×10^{-8}	0.91
II	a	1.00×10^{-3}	3.0×10^{-7}	0.80
II	b	2.47×10^{-3}	3.0×10^{-7}	0.97

* No inactive manganese was added to the stock solution and so its manganese concentration was unknown.

TABLE II. *Effect of initial concentration of manganese on the fraction codeposited with lead dioxide*

Cell	Run	Initial concentration, M		Fraction of manganese codeposited
		Manganese	Lead	
IV	a	1.4 ml tracer*	7.7×10^{-4}	0.60
I	a	3.7×10^{-8}	7.7×10^{-4}	0.70
III	a	3.8×10^{-8}	7.7×10^{-4}	0.68
II	a	1.9×10^{-7}	7.7×10^{-4}	0.69
IV	b	4.3 ml tracer*	2.31×10^{-3}	0.71
III	b	3.0×10^{-8}	2.31×10^{-3}	0.89
I	b	1.2×10^{-7}	2.31×10^{-3}	0.93
II	b	2.4×10^{-7}	2.31×10^{-3}	0.96

* No inactive manganese was added to the stock solution and so its manganese concentration was unknown.

where only tracer manganese was used, the fractional coprecipitation was significantly lower.

Coprecipitation of silver.—In order to examine briefly the possibility of coprecipitating other elements in a selective way, qualitative experiments were made with carrier-free silver (8). Using 180 ml portions of 0.1M $HClO_4$ containing silver-111 tracer and a 13 cm^2 platinum gauze anode, duplicate electrolyses were carried out successively for 1 hr at 0.10 v intervals from +1.50 to +2.00 v (vs. S.C.E.). At the end of each hour, the fraction of silver remaining in solution was determined by withdrawing duplicate 0.100 ml aliquots, evaporating to dryness on 1-in. watch glasses, and counting the radioactivity. The average range of the duplicates was less than 3% of the total count.

No deposition of silver was detected over the range from +1.50 to +2.00 v. However, after completion of the electrolysis at +2.00 v, 200 mg of lead was added (as 1.0 ml of lead nitrate solution) and the electrolysis continued for 3 hr at 2.00 v. At the end of that time, 96% of the silver had codeposited with lead dioxide in each cell.

Without removing the electrodes, the deposits were dissolved by allowing the electrodes to stand overnight with no potential applied. Repetition of the electrolyses at 0.1 v intervals showed that, although lead began to deposit at +1.35 v, no silver was deposited until +1.90 v. After 30 min at this potential, 25% of the silver had deposited. The potential was then changed to +2.00 v. After 30 min at this potential, 50% of the silver had deposited; after 3

TABLE III. *Effect on the manganese-lead dioxide exchange of opening the electrical circuit*

	% of Manganese deposited	
	Electrolytic coprecipitation	Coprecipitation plus exchange (open circuit)
I a	80	98
b	93	99
II a	80	97
b	97	99
III a	74	97
b	90	98
IV a	60	93
b	71	97

hr, 95%. Since potentials more positive than +2.0 v result in lower current efficiency due to concurrent oxygen evolution, the use of +2.0 v would appear to be close to optimum for making separations.

Discussion

It is clear from the results of this study, that the electrode potential was a major factor which controlled the anodic coprecipitation of manganese and of silver with lead dioxide. However, no quantitative statements can be made as yet. It appears that a relationship(s) analogous to those of Berthelot-Nernst and Doerner-Hoskins (9), which are used in chemical coprecipitation, should be applicable to electrolytic coprecipitation. However, the attainment of equilibrium conditions required by the former appears to be virtually impossible, especially when appreciable amounts of deposit are involved, because of the limited surface area of the deposit. With regard to the Doerner-Hoskins distribution, the condition that the composition of the outer layer of the deposit be proportional at all times to that of the solution would be attainable only in special cases.

In both expressions for chemical coprecipitation, the fractional coprecipitation of the trace depends on the fractional precipitation of the carrier, but is independent of the initial concentrations of both trace and carrier. The data in Table I and Fig. 4 show that the fractional electrolytic coprecipitation of a trace under the prescribed conditions was independent of the fractional precipitation of the carrier but strongly dependent on the initial concentration of the carrier. Thus, larger concentrations of lead resulted in more nearly complete precipitation of manganese. Unfortunately, the data in Table II indicate no clear-cut effect of changes in the initial concentration of manganese upon its fractional coprecipitation. In any event, it is clear that the electrolytic process of coprecipitation is affected by experimental variables in a way different from the chemical process.

It is clear from runs 4a and 4b in Fig. 4 that the exchange of manganese in solution with lead in the electrode did not take place at an appreciable rate as long as the electrical circuit was closed. It was, therefore, interesting to note that rapid exchange occurred upon opening the circuit. Table III shows the results obtained by disconnecting the anode after each of the runs in Fig. 4 and allowing it to remain in contact with the solution for 12 hr. In each case analyses showed that much of the lead dioxide had redissolved while most of the manganese had deposited. These few experiments would appear to indicate that a mechanism like the following might be operating:

$$Mn^{2+} + Pb^{4+} = Pb^{3+} + Mn^{3+} \text{ (rapid)} \quad (I)$$

$$Pb^{3+} \text{ (at electrode)} = Pb^{4+} + \text{electron (rapid)} \quad (II)$$

$$Pb^{3+} + Mn^{3+} = Pb^{++} + Mn^{4+} \text{ (slow)} \quad (III)$$

Reaction (I) could occur whether the circuit were open or closed. At open circuit, reaction (III) would be able to proceed, whereas reaction (II) could not. Trivalent manganese could disproportionate to the divalent and tetravalent states, but if this took place, it must have been at the electrode surface because most of the manganese was found in the deposit.

Further studies are now in progress to evaluate in more detail the effect of different experimental variables on the coprecipitation and to explore the possibilities of obtaining more nearly quantitative electrolytic coprecipitation of the trace.

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1957 Journal.

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Use of Radioactive Mercury to Study the Relation of Mercury to Depreciation of Fluorescent Lamps

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ABSTRACT

Radioactive mercury was used to determine whether there is any relationship between the depreciation of fluorescent lamps and the amount of mercury picked up on the lamp walls during lamp operation. It was found that early in lamp life there is no such relationship. However, after 1000–2000 hr, depending on the phosphor type, a relationship was established.

It has been postulated (1, 2) that mercury in one form or another is responsible for the darkening of fluorescent (F-) lamps. Some authors (3, 4) have discussed the interaction between mercury and the fluorescent powder and proposed reaction mechanisms. Attempts have even been made (5) to restrict the effect of mercury on depreciation to a specific period of the lamp life.

It was never shown, however, that there is any quantitative relationship between the mercury uptake and depreciation. This is because regular analytical methods of determining mercury uptake are difficult, are subject to many errors, and necessitate the use of a large number of samples to make the results meaningful. One must also destroy the lamp each time an analysis is made and so only one determination per lamp is possible.

With radioactive mercury (Hg 203), however, it was felt worthwhile to carry out an experiment which might provide unequivocal information about the relation of mercury to F-lamp depreciation. This isotope has a half-life of 44 days and emits beta and gamma rays of 200 and 300 electron kv, respectively. The use of this radioactive isotope enables one to follow mercury pick-up along with depreciation in a single nondestructive test. Also, possible errors in manufacturing a lamp could not influence the relationship between mercury and depreciation for that particular lamp. Therefore, this method enables one to study a variety of aspects of depreciation as related to the mercury pick-up. Effects of impurities (in the filling gas or phosphor), additives, and manufacturing processes might be successfully investigated. However, in the following experiment the authors restricted themselves to a study of the effect of phosphor type on mercury absorption.

DESCRIPTION OF EXPERIMENT

Lamp manufacture.—Standard 40 watt F-lamp bulbs were coated with suspensions of the following four phosphors: zinc silicate (activated with Mn^{+2}), calcium silicate (activated with Pb^{+2} and Mn^{+2}), magnesium arsenate (activated with Mn^{+4}), and magnesium lithium arsenate (activated with Mn^{+4}). Standard techniques for preparation of suspensions and for coating were used.

The lamps were prepared in the following way. The mercury-containing tube was sealed to the lower exhaust stem of the lamp. An oven which was vertical and short enough to allow the lower exhaust stem to protrude was put around the lamp and the lamp exhausted with no mercury dosage. Heat was applied for 5 min at 400°C. Cathodes were activated according to the standard schedule for rapid start lamps. There was, of course, no end glow. The lamp was flushed with 5 mm of argon and cooled. Mercury was then torched up from below and the bottom exhaust stem sealed about 2 in. from the lamp. Argon was introduced at about 3 mm and the lamp sealed off. The bottom stem was tipped off close to the flare and both ends based. After a number of trial runs, 9 radioactive lamps were made in this way. Eight lamps were manufactured in sets of two, with each set having a different phosphor. An additional variable was incorporated in the ninth lamp which was coated with heavily overmilled zinc silicate (24 hr of milling).

Measuring procedure.—It was assumed that mercury might deposit on the phosphors in three possible ways: (*a*) as droplets, (*b*) as a loosely adsorbed surface layer, and (*c*) as a tightly absorbed layer.

Since it has been shown that droplets cannot be related to depreciation (3), it was decided to remove them to the lower end of the lamp. This was done as soon as the lamps were finished and photometered in the standard way. The mercury was driven to the lower end by heating the upper three quarters of the lamp at about 90°C for 3 hr. Care was taken in all subsequent operations to position the upper end of the lamps above the lower in order to keep all the liquid mercury at the bottom.

To make sure no droplets were left at the top end of the lamp, x-ray, no-screen film (du Pont #508) was wrapped around the bulb and left on for 18 hr. With a rough calibration it is possible to make an estimate of the minimum size of radioactive mercury droplet which would be required to give a trace. Such an estimate has been made in Appendix I and indicates that the particles, if any, on the walls of the lamp at the upper end, must have been less than about 20 μ in diameter. Therefore, in all this work concern was only with loosely and tightly held Hg. The latter was defined as that which is held by the phosphor so strongly that it cannot evaporate into the arc even if all the vapor above it has been removed to the point where the discharge is characteristic of pure argon.

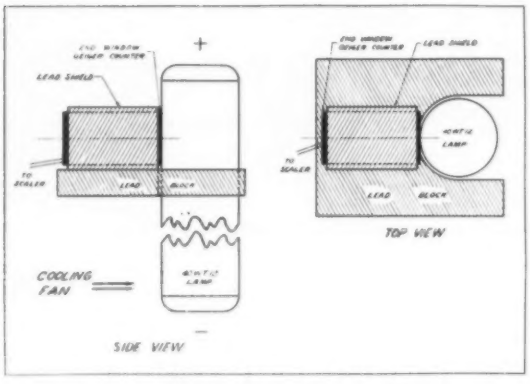

FIG. 1. Schematic diagram of apparatus

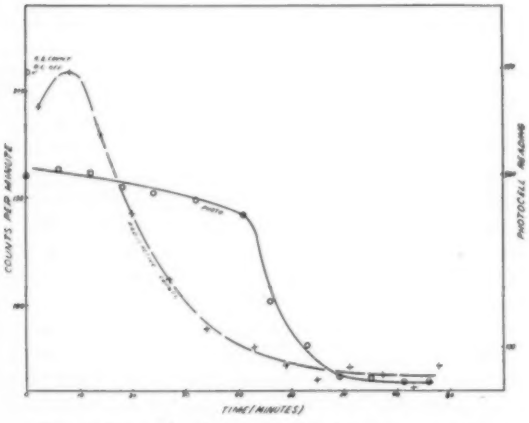

FIG. 2. Example of data obtained in d-c operation

The removal of vapor-phase Hg was achieved by operating the lamp on direct current. The bottom ends were held negative and cooled with a fan. A counting rack was supplied with 250 volts d.c. The lamp was started with a spark coil and a photocell applied periodically to the area of the lamp under investigation. The photocell current was read by means of a G.E. galvanometer. As the Hg vapor was pulled down and away from the photocell area, the light output eventually dropped quickly. No external heating of the lamp was applied during these operations. Various counting and detection methods were tried. The final set-up for counting is sketched in Fig. 1. A Nuclear Chicago Scaler Model 172 was used with a Nuclear Chicago #34 end-window beta counter. Five-minute counts were made alternately with the photocell introduced in place of the Geiger counter. This procedure of d-c counting was carried out each time after operating the lamps under a.c. for 0, 100, 500, and 1500 hr.

Results and Observations

Observation under d-c operation.—A typical graph obtained under d-c operation is given in Fig. 2. Although initially the counting data were somewhat erratic, at 500 and 1500 hr of a-c burning the curves were relatively smooth. The only deviation from a monotonic decrease was a slight rise in count rate immediately after a lamp was started on d-c operation and had burned for a few minutes.

In the case of two phosphors, i.e., magnesium arsenate and zinc silicate, fairly steep slopes in the count-rate curve were observed at the beginning of d-c operation. That this rapid drop in count rate was not due to a decrease in the amount of mercury in the vapor phase was shown by estimating how much the latter could contribute to the count rate. The calculations on which the estimate was based are given in Appendix II and show that the contribution due to the vapor was at the most no more than room background.

Furthermore, the mercury concentration in the vapor phase remained approximately constant, in spite of the rapid drop in count rate. This was shown by the initial steadiness of the light output as measured by the photocell.

This confirmed the preliminary hypothesis that Hg could be held loosely on the walls of the lamp. The light output remained constant as long as the vapor phase removed by d.c. was compensated by the Hg evolution from the phosphor. When this was no longer the case, the light output dropped radically (see the photocurve of Fig. 2).

The fact that a distinct point could be reached in these counting and photocell observations where insufficient Hg was available for the maintenance of light does not necessarily mean that the remainder of the mercury on the wall was tightly held. It should be emphasized, however, that the mercury remaining on the lamp wall proved to be held far more tenaciously after the light drop than before. This can be seen by comparing the initial steepness with the final slope of the count-rate curve in Fig. 2. To check on the possibility of a further change in the final slope with time, a lamp was left running under d-c operation for 18 hr. There was little change in count rate.

Relatively heavy overmilling of the zinc silicate phosphor had little effect on the Hg adsorption.

Tightly Held Mercury

The most important of the large mass of data accumulated in this experiment have been collected in Table I. It was assumed that no mercury was tightly held at zero hours.

For all phosphors, the amount of tightly held Hg increased with time of burning. Further, more of this mercury was taken up per hour in the first 100 hr than in the remainder of the time. It is also evident that different phosphors held (tightly) quite different amounts of mercury, e.g., after the lamps burned for 1500 hr, magnesium arsenate held about six times as much as calcium silicate.

There was remarkable agreement between lamps of the same phosphor. Striking exceptions, however, were the lamps with the magnesium lithium arsenate. For some reason, one of these lamps depreciated much more than the other and also picked up more mercury.

In analyzing these results, various ways of relating depreciation to mercury uptake in the phosphors were tried. Plots were made against time of burning for different functions of R, (the tightly held mercury) and L_i, (the lumen

TABLE I. *Lumens and relative mercury uptakes against hours of lamp burning*

Lamp code No.	0 Hr		100 Hr			500 Hr			1500 Hr		
	lumens	Relative "loose" Hg	lumens	Relative "loose" Hg	Relative "tight" Hg	lumens	Relative "loose" Hg	Relative "tight" Hg	lumens	Relative "loose" Hg	Relative "tight" Hg
GR13	3560	15	3154	168	47	2632	180	100	2000	128	152
GR10	3460	29	2938	196	61	2388	400	107	1892	215	155
GR2, 11	3070	2	2808	160	46	2364	128	106	1900	140	200?
CS13	2000	11	1825	10	34	1777	4	76	1670	55	140
CS14	1935	32	1793	107?	37	1746	20	82	1634	30	160
MgAs9	634	11	478	12	120	416	130	320	261	1440	860
MgAs11	600	37	485	16	111	433	196	354	268	920	900
MgLiAs5	513	12	511	48	59	478	41	155	380	15	377
MgLiAs4	568	10	476	56	60	402	175	211	270	146	556

Phosphor type:	GR	GR2	CS	MgAs	MgLiAs
	Zinc silicate	Overmilled zinc silicate	Calcium silicate	Magnesium arsenate	Magnesium lithium arsenate

Notes: 1. "Loose" Hg = DC off (t) − Tight Hg. 2. "Tight" Hg = Final Level (t).

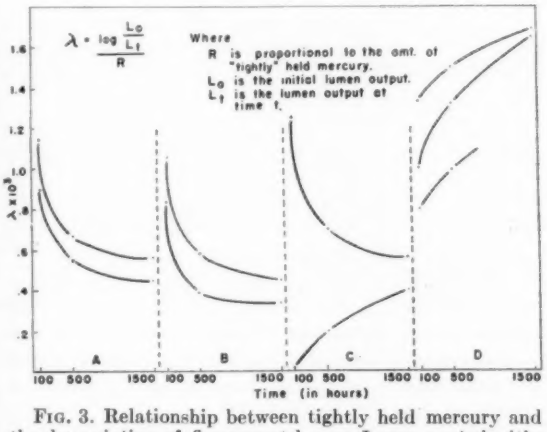

FIG. 3. Relationship between tightly held mercury and the depreciation of fluorescent lamps. Lamps coated with: A, calcium silicate; B, magnesium arsenate; C, magnesium lithium arsenate; D, zinc silicate.

output at time t). Probably the best description of the situation is given in Fig. 3 in which the ratio is plotted,

$$\lambda = \left(\frac{\log L_0/L_t}{R}\right)$$

Should λ prove to be constant with time a direct relation will have been established.

A study of Fig. 3 brings out clearly the fact that no definite relationship exists in the first 1000 hr or so between tightly held mercury and the depreciation of these lamps. Again, the fortuitous difference in behavior between the two magnesium lithium arsenate lamps is useful in that it emphasizes this point. The very poor magnesium lithium arsenate lamp has initially a very high λ which means a high depreciation per unit Hg uptake. This is true for the poor magnesium arsenate lamps as well, whereas the calcium silicate lamps have similar curves and yet depreciated very little. On the other hand, the good magnesium lithium arsenate lamp displays a curve similar to the green GR lamps which are relatively poor. Further evidence of the lack of a relationship of tightly held Hg to lumen drop in the first 1000 hr is seen, for example, in the results of the lamp # MgLiAs5 given in Table I. At 100 hr the "tight" Hg reading was as high as 59 even though there was no depreciation.

Because the lamps were manufactured as much as possible in the same way, the large difference in the λ's for the two magnesium lithium arsenate lamps is most likely due to small amounts of residual impurities as a result of improper lehring and exhaust. It seems reasonable, therefore, to conclude that in some cases the depreciation is governed in the first 1000 hr solely by impurities rather than by either Hg uptake or phosphor type.

In contrast to the preceding observations, for all phosphors λ approaches a constant after 1000 hr of burning. This point is particularly well demonstrated again by the two magnesium lithium arsenate curves. Although the lamps exhibited entirely different behavior, their λ curves approach each other asymptotically at $t > 1500$ hr. Thus, eventually, there does seem to exist a relation between the residual tightly held Hg and lumen output of the form:

$$L_t = L_0 e^{-\lambda R}$$

It should be noted that there is no experimental information about the behavior of these lamps after 1500 hr. Therefore, one is not actually justified to conclude with certainty that λ will not change at some future time in lamp operation. However, it is well known that after 1500 hr fluorescent lamp characteristics are substantially stable and change, if at all, very slowly with time. In fact, for some of these lamps, e.g., those with magnesium arsenate, λ proved to be constant within experimental error for as much as 1000 hr of burning, making it extremely unlikely for a change to occur later. Furthermore, the two magnesium lithium arsenate curves, although exhibiting ini-

TABLE II. *Comparison of lumens and tightly held* Hg *after baking and burning lamps for 100 hr*

Lamp No.	1500 Hours		Baked		100 Hours later		Remarks
	Lumens (1)	Tight Hg (2)	Lumens (3)	Tight Hg (4)	Lumens (5)	Tight Hg (6)	
GR13	2000	152	2216	336 (?)	2055	140	Baked at 300°C no fan
GR10	1895	155	2324	71	1990	125	Baked at 350°C with fan
MgAs9	261	860	470	96	343	345	Baked at 350°C with fan
MgLiAs5	380	377	475	110	446	137	Baked at 350°C with fan

Note: Lumen change $\propto$ Hg, e.g., for GR10, $\frac{(3)-(1)}{(2)-(4)} \cong \frac{(3)-(5)}{(6)-(4)}$.

tially completely different slopes, still approach the same value, thus strongly suggesting no further change in λ.

Since λ is very small, $\sim 10^{-3}$, the relation may well be linear (i.e., $L_t = L_0 (1 - \lambda R)$. Assuming that the tightly held Hg causes depreciation by absorbing radiation, then a true linear relation would imply that this is a surface phenomenon. In other words, mercury is held tightly to the surface and acts only to screen the radiation. At 1500 hr as much as 50% of the phosphor surface might be covered by a monoatomic Hg layer (*see* Appendix III). If all this mercury were deposited on the surface of the phosphor next to the arc, the depreciation would certainly be significant and the relation linear.

However, should the mercury be taken up in the depth of the phosphor layer or within the individual particles, the relation would be logarithmic since the earliest absorption of Hg would tend to have the greatest effect.

If the mercury is indeed distributed throughout the phosphor layer, some of it could penetrate to the glass wall and be absorbed there. To check this possibility, an 8-in. section was cut from each lamp about 1 ft from the top end, using the proper precautions to avoid radiation hazard and taking care not to disturb the phosphor. A small Geiger tube was centered within the section and the radiation counted for 5 min. The section was then washed with dilute followed by concentrated nitric acid and a similar count made again. The washing was carried out a couple of times to insure complete removal of the phosphor and its mercury.

The results of this experiment showed definitely that between 10 and 20% of the mercury on the wall was retained in the glass itself, at least to the degree that it could not be removed by successive washings with nitric acid.

This information leads to the conclusion that the relation is more likely to be logarithmic, but it does not tell whether the mercury has actually penetrated the phosphor particles. To resolve this question an attempt was made to determine the order of magnitude of the activation energy for desorption of the tightly held mercury. Several lamps were heated using a vertical oven with 10 in. of the lower end of the lamp protruding and being cooled by a fan. The lamps were heated for approximately 2–3 hr at 300°–350°C. A 5-min count was carried out immediately upon cooling. The lamps were photometered in the usual way, burned vertically on a.c. for 100 hr and photometered again. They were finally counted in the usual d-c operation.

The results given in Table II show fairly well that residual mercury is held quite tightly, requiring at least 350°C to be dislodged. This activation energy is about half that necessary for the preparation of phosphors (about 1400°K). Thus, the phosphor-Hg binding energy is fairly high and therefore the Hg is more likely to be within the particle.

It should also be noted that there is a strong indication of the proportionality of tightly held mercury to lumen drop. The extra 100 hr burning effects a remarkably quick pickup or recovery of the tightly held mercury. This is, of course, associated with the characteristic rapid drop in lumens under such conditions.

The fact that a relation exists, however, does not prove that Hg is actually a primary cause of depreciation even after 1500 hr. There are three possible ways in which a relationship could arise.

(*A*) Hg may be the primary responsible agent, i.e., as indicated above, it may have a straightforward screening action. If this is the case, λ should be identical for all phosphors. In Fig. 3, however, note that $\lambda > 1500$ for the zinc silicate is at least 3 to 4 times greater than for the other lamps. This eliminates the first possible reason.

(*B*) Lumen-loss may be caused by Hg pickup which, in turn, is the result of some other primary agent (say, crystal imperfections). In this case it is reasonable to assume that λ is a function of the primary agent only. That enough Hg is present on the walls of the lamp to cause depreciation directly is shown in Appendix III.

(*C*) Hg pickup might be simply a side effect of lumen depreciation actually caused directly by another agent. The experiment of the authors cannot distinguish between case (*B*) and (*C*).

Loosely Held Mercury

It was evident as early as at 100 hr that some lamps picked up more loose mercury than did others (*see* Table I). This became much more definite as the lamps burned. Lamps which showed the greatest eventual depreciation tended to take up the largest amounts of loosely held mercury. This can be seen, for example, if one compares poor magnesium arsenate and zinc silicate coated lamps with the lamps coated with calcium silicate. In the case of magnesium lithium arsenate the lamp with abnormally high depreciation characteristics (code number MgLiAs4) also showed higher concentrations of loosely held mercury than the better lamp (code number MgLiAs5).

Thus, the amount of loose mercury seemed to be a good symptom of how poor the lamp was in terms of depreciation. It was not possible, however, to obtain any quantitative correlation.

To determine whether there was any direct effect of

loosely held mercury on depreciation, lamps were photometered immediately before and after d-c operation at 100 hr. During the d-c operation, the mercury was pulled down from the upper half of the lamp. Although the lamps had depreciated in the first 100 hr of their burning by as much as 30%, there was no significant difference in the photometric results before and after the d-c operation. Thus it is concluded that loosely held mercury cannot be responsible for depreciation.

Even though the loose mercury is an indication of the depreciation which has occurred in the lamps in the first 1000 hr or so of burning, such a relation is not quantitatively evident for the tightly held mercury. However, as noted before, the amount of tight mercury does increase also with burning. This is natural because larger amounts of loosely deposited Hg should produce, by diffusion, larger deposits of tightly held Hg.

Conclusions

A nondestructive experiment with little hazard has been designed, using Hg 203, to determine the relative amounts of mercury takeup by various phosphors. The following information was obtained.

In the first 1000 hr or so of burning there is no evident relation between tightly held Hg uptake and depreciation.

The loose Hg uptake is a strong symptom of the depreciating tendency of a lamp, but cannot be the direct cause.

After 1000 or so hours there exists a direct relation between tightly held Hg and depreciation. Whether the Hg at this time is an effect of, or a cause of, depreciation cannot be determined explicitly from this experiment.

Over 10% of the tightly held mercury is retained in the glass itself and cannot be removed by nitric acid.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1957 Journal.

APPENDIX I

Estimate of Size of Hg *Droplets Detectable by Autoradiography*

Calibration of the x-ray film showed that about 10 milliroentgens (mr) were required to give detectable density.

The output at a meter (6) from one millicurie of Hg 203 is about 0.15 mrhm.

Thus, to obtain 10 mr at 1 mm (glass wall thickness) after 18 hr exposure there is required

$$\left(\frac{10\text{ mr}}{0.15\text{ mrhm}}\right)\left(\frac{1\text{ mm}}{1\text{ meter}}\right)^2\left(\frac{1}{18}\right) \approx 3.5 \times 10^{-6}\text{ mc}$$

The specific activity of the sample was 1 mc/50 mg. $\therefore$ 3.5×10^{-6} mc corresponds to $3.5 \times 10^{-6} \times 50 = 0.2\ \mu$g. The density of Hg is 14 g/cc.

$$\therefore 0.2\ \mu\text{g} = \frac{0.2 \times 10^{-6}}{14} \approx 10^{-8}\text{ cc}$$

The radius of a spherical droplet of this size is the order of 10^{-3} cm or 10 μ.

APPENDIX II

Estimate of Count Rate Due to Hg *Vapor*

The following calculations yield an estimate of the count rate obtained (by the apparatus of Fig. 1) as a result of the Hg initially present in the vapor phase of the lamps.

The total Hg in the form of vapor (8 μ) amounts to about 0.1 mg, volume of lamp is 1200 cc, specific activity of Hg 203 is 20 mc/g.

$$\therefore \frac{0.1 \times 10^{-3}}{1200} = 0.8 \times 10^{-7}\text{ g/cc}$$

and $0.8 \times 10^{-7} \times 20 = 16 \times 10^{-7}$ mc/cc.

The volume viewed by the GM counter is 20 cc, but not all of this volume contributes equally to the count rate. The size of the contribution due to any element of volume depends upon the solid angle it subtends at the counter, i.e., on how near it is. Dividing the volume into layers perpendicular to the counter axis and adding up the solid angles due to each layer shows that the "geometry" is about 5%. This means that the counter can receive only $0.05 \times 16 \times 10^{-7} \times 20 = 16 \times 10^{-7}$ mc.

The counter, in turn, does not respond to every gamma ray which enters. In fact, the efficiency of the beta counter is only 0.1% for rays of 0.3 mev energy (7).

Thus, the counter records only about 16×10^{-10} mc. One mc = 2.2×10^9 counts/min. The count rate due to the vapor phase is therefore estimated to be about $16 \times 10^{-10} \times 2.2 \times 10^9 = 3.5$ counts/min. This should be compared with the background count rate of 13 counts/min.

APPENDIX III

Estimate of Amount of Hg *on Walls after 1500 Hr*

There are approximately 200 counts/min from 6 cm^2. If one assumes 50% geometry and a counter efficiency of 0.1%, this corresponds to

$$\frac{200 \times 2 \times 10^3}{60} \approx 7000\text{ disintegrations/sec}$$

or about 0.16 microcuries/6 cm^2, i.e., about 0.03 μc/cm^2.

The specific activity is 20 mc/g and therefore one has $\frac{0.03 \times 10^{-3}}{20}$ or about 1.5 μg/cm^2.

Since the number of atoms in 200 g of Hg is 6×10^{23}, 1.5 μg/cm^2 corresponds to

$$\frac{1.5 \times 10^{-6}}{200} \times 6 \times 10^{23} = 5 \times 10^{15}\text{ atoms/cm}^2$$

If one takes the diameter of a Hg atom to be 3Å one can spread out $\left(\frac{10^8}{3}\right)^2$ or about 10^{15} atoms on 1 cm^2. Thus one would have about 4 to 5 atomic layers if the surface were perfectly flat. Actually, the phosphor surface has 10 to 100 times the area of the flat glass surface. This means that one could have only as much as one-half of an atomic layer present on the walls of the lamp.

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Cathodic Reduction of 3,4,5,6-Tetrachloro-*N*-(2-Dimethylaminoethyl)-Phthalimide

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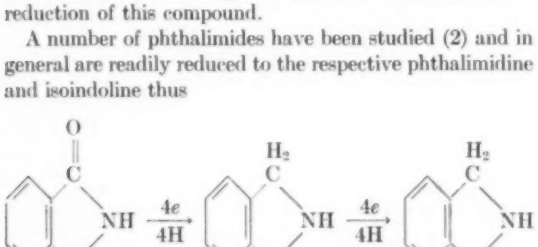
ABSTRACT

The cathodic reduction of 3,4,5,6-tetrachloro-*N*-(2-dimethylaminoethyl)-phthalimide to its respective isoindoline has been studied using a cadmium, lead, and mercury electrode. With the aqueous CH_3COOH–H_2SO_4 medium used, the electrode overpotentials were higher than in an aqueous H_2SO_4 medium. This contributed to obtaining higher efficiencies in the reduction process. The best yield and current efficiency was obtained using a lead cathode and a current density of 0.0493 amp/cm². The current efficiency obtained under constant current density conditions was improved considerably by use of controlled potential electrolysis at −1.10 v vs. S.C.E. At a potential of −0.68 v vs. S.C.E. the partially reduced product, 4,5,6,7-tetrachloro-2(2-dimethylaminoethyl)-3-hydroxyphthalimidine, was obtained.

The reduction of 3,4,5,6-tetrachloro-*N*-(2-dimethylaminoethyl)-phthalimide to the respective isoindoline and isolation as its dimethochloride derivative has been achieved using lithium aluminum hydride as the reducing agent (1). However, because of the low solubility of this substituted phthalimide in the solvents usually used in this chemical reduction with consequent low yield of product, it was decided to investigate the use of electrolysis for the reduction of this compound.

A number of phthalimides have been studied (2) and in general are readily reduced to the respective phthalimidine and isoindoline thus



Although the reported yields of the isoindolines obtained were usually satisfactory, the current efficiency based on the yield of product was quite low. This low efficiency can be attributed to the following: in the medium commonly used, namely aqueous-H_2SO_4, the overpotential of the cathode was too low for the current densities used; as a consequence there was a large quantity of gas evolved at the cathode. Another reason for the low efficiency obtained by previous workers was that in many cases the depolarizer was not immediately soluble in the medium. As the limiting current depends on the concentration of the depolarizer, the current densities used were too high and, as a result, the excess current was utilized for the production of hydrogen gas.

The object of these experiments was, first, to develop a medium which would be both a good solvent for the 3,4,5,6-tetrachloro-*N*-(2-dimethylaminoethyl)-phthalimide and at the same time increase the overpotential of the cathode to that at which improved reduction efficiency could be obtained; second, to compare the effectiveness of various high overpotential electrodes such as cadmium, lead, and mercury for the preparation of 4,5,6,7-tetrachloro-2-(2-dimethylaminoethyl)-isoindoline; third, to compare the efficiency of the reaction at constant current density under the most ideal conditions with that obtained using controlled potential electrolysis; and, last, to determine the reaction path from the phthalimide to the isoindoline.

It has been reported (3) that the overpotential of the various cathodes studied is higher in a glacial CH_3COOH-H_2SO_4 medium than in an aqueous-H_2SO_4 medium. The tetrachlorophthalimide was quite soluble in this medium; however it could not be used as such, first, because the electrical resistance was too high, and, second, because the desired isoindoline was not obtained when the electrolysis was performed in this medium. It was found, however, that the substituted phthalimide was soluble in an aqueous solution containing CH_3COOH and H_2SO_4, for example 40% by volume of CH_3COOH and 12% by volume of H_2SO_4. The cathode potential vs. S.C.E. was determined for each of the electrodes used at the current densities which gave the optimum yields of isoindoline. These potentials were found to be higher in this medium than under comparable conditions in the aqueous H_2SO_4 medium. This was also indicated by the absence of hydrogen gas evolution at current densities at which gas evolution was obtained in an aqueous H_2SO_4 medium.

Experimental

Electrodes.—The cadmium electrode whose area was 78 cm² was prepared from pure sheet cadmium and subjected to pre-electrolysis in the aqueous-acetic-sulfuric acid prior to use. The 64.9 cm² lead electrode was purified by Tafel's method (4); the mercury was reagent grade. A platinum electrode served as the anode in all experiments.

Cells.—The cell used with the mercury cathode was

similar to that previously described (5). This gave an electrode area of 23.93 cm². The solid electrodes were used in a cell consisting essentially of two Pyrex pipe elbows held together by bolted flanges (Fig. 1). An Amberplex C-1 ion exchange membrane (Rohm and Haas Co., Philadelphia, Pa.) (E) was used to separate the anolyte from the catholyte. This membrane was chosen as a result of extensive tests to find a membrane which would give excellent conductivity with a minimum amount of diffusion. Thus it is possible to use a nonaqueous or partially aqueous working medium which, in this instance, is the catholyte and an aqueous nonworking medium The over-all result is a considerable improvement in conductivity when using the nonaqueous or partially aqueous systems so often needed to obtain solutions of organic substances. The cathode side of the cell contained a stirrer (A), thermometer (B), and the electrode (C) which was curved so as to make contact only with the glass along the electrode edge. This resulted essentially in a floating electrode whose lower surface was not shielded from current flow. Thus the current concentration was essentially the same on both surfaces. A saturated calomel reference electrode (F) was in contact with the working cathode through a salt bridge (G) in instances in which controlled potential conditions were utilized. The source of contact between the salt bridge and the working electrode consisted of a rubber policeman attached to the end of the glass bridge. The edge of the rubber policeman which makes contact with the working electrode is pierced with numerous asbestos fibers. The anode portion of the cell contained a platinum electrode (D). The whole cell was immersed in a bath for cooling or heating as dictated by the current density to maintain a temperature of 50°–55°C. This temperature gave the desired solubility to the concentration of depolarizer used.

Power supply.—The apparatus used for the controlled potential electrolysis was similar to that previously described (6). To use this instrument as a constant current device required the insertion of a 0.1 ohm resistor between the cathode lead and the cathode. The reference electrode lead is connected directly to the cathode. Current output is then controlled by the reference potential rheostat.

Electrolysis media.—In the cell used in conjunction with the cadmium or lead electrode, the catholyte consisted of 6.5 g of 3,4,5,6-tetrachloro-*N*-(2-dimethylaminoethyl)-phthalimide, 30 ml glacial CH_3COOH, 36 ml distilled water, and 9 ml concentrated H_2SO_4; the anolyte, 9 ml concentrated H_2SO_4 in 66 ml distilled water. The catholyte in the mercury cathode cell consisted of 5.2 g of the phthalimide, 24 ml glacial CH_3COOH, 28.8 ml distilled water, and 7.2 ml concentrated H_2SO_4.

Constant current density electrolysis.—The various current densities used are approximate multiples and fractions of an arbitrary limiting current (*Li*) obtained from the equation developed by Nernst (7) for electrolytic processes in which diffusion is the rate-determining step.

$$Li = 0.0223\ DCn$$

A value of 0.6 cm^{-2} day^{-1} was an arbitrary diffusion coefficient (*D*) assigned to the phthalimide on the assumption that it would be somewhat less than quinone. The concentration *C* in g moles/liter was 0.2435 and $n = 8$ based on

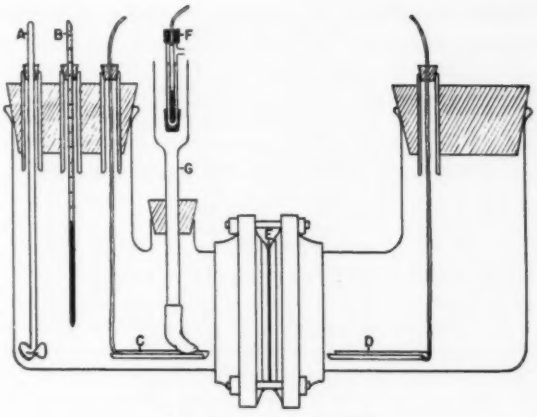


FIG. 1. Electrolysis cell

the fact that an 8-electron change occurs in going from the phthalimide to the isoindoline. Correction of the limiting current obtained for use at 55° gave a value of 0.0492 amp. No correction was made for agitation as it was thought the phthalimide was too slow a depolarizer to have this correction make any significant difference, especially as the limiting current value was merely an arbitrary focal point.

Procedure

4,5,6,7-Tetrachloro-2-(2-dimethylaminoethyl)-isoindoline and 4,5,6,7-tetrachloro-2-(2-dimethylaminoethyl)-phthalimidine.—Preliminary experiments indicated that it was necessary to pass at least twice the theoretical amount of current, calculated on the basis of an 8-electron change, to obtain the maximum yield under ideal conditions. Therefore, in all constant current density experiments in which 6.5 g of the depolarizer was used, 28,100 coulombs were passed and where 5.2 g was used, 22,530 coulombs were passed.

The products of electrolysis were isolated by making the catholyte, which had been first diluted with an equal volume of water and chopped ice, basic with aqueous NaOH. The precipitate which formed was extracted with ether, the ether extracts washed with water, dried over anhydrous Na_2SO_4, filtered, and then evaporated. The residue was triturated with warm pentane. In those experiments wherein the lower yields (less than 88%) of the completely reduced product was obtained, there was a partially reduced pentane-insoluble fraction which was 4,5,6,7-tetrachloro-2-(2-dimethylaminoethyl)-phthalimidine (III). Recrystallization of this product from ethanol gave white needles, m.p. 166°–67° (corr.); anal. found: C, 42.64; H, 3.70; N, 8.24; Cl, 41.29%. $C_{12}H_{12}ON_2Cl_4$ requires C, 42.33; H, 3.54; N, 8.19; Cl, 41.47%.

The fraction which was pentane soluble, 4,5,6,7-tetrachloro-2-(2-dimethylaminoethyl)-isoindoline (IV), was recovered by evaporation of the solvent. The oily residue on cooling formed platelets, m.p. 66–68° (corr.). Recrystallization from a small quantity of pentane gave pale yellow platelets, m.p. 69°–71° (corr.); anal. found: C, 44.22; H, 4.37; N, 8.48; Cl, 43.30%. $C_{12}H_{14}N_2Cl_4$ requires C, 43.93; H, 4.31; N, 8.54; Cl, 43.24%.

In all experiments it was possible to account for more

TABLE I. *Effect of current density on yield of isoindoline with various electrodes*

Cathode	C.D. (amp/cm²)	% Yield isoindoline	Current eff.
			%
Cd	0.0243	38.2	19.1
	0.0487	37.7	18.9
	0.0730	50.6	25.3
	0.0974	49.4	24.7
	0.1461	52.2	26.1
	0.1948	40.4	20.2
Pb	0.0243	90.5	45.2
	0.0493	91.1	45.6
	0.0770	56.4	28.2
	0.1190	53.9	27.0
	0.1540	52.0	26.0
	0.1950	39.6	19.8
Hg	0.0501	58.7	29.4
	0.1002	64.3	32.1
	0.1504	66.8	33.4
	0.2005	79.7	39.8
	0.2507	74.3	37.2
	0.3008	70.6	35.3

than 90% of the starting material based in the quantity of the phthalimidine and/or the isoindoline isolated.

Results obtained at the various current densities studied with cadmium, lead, and mercury are summarized in the Table I.

Controlled Potential Electrolysis

The potentials used in the following experiments were obtained from a voltammetric curve, the lower potential being approximately 0.1 v above that potential at which the current began to increase above the residual current. The higher potential was approximately 0.1 v below that which resulted in gas evolution at the electrode surface.

4,5,6,7-Tetrachloro-2-(2-dimethylaminoethyl)-isoindoline (IV).—The cathode used was a lead sheet whose area was 78 cm² previously treated according to Tafel's method and subjected to pre-electrolysis as a cathode in the aqueous-CH_3COOH-H_2SO_4 medium. The catholyte consisted of 6.5 g of the tetrachloro-phthalimide, dissolved in a solution of 30 ml glacial CH_3COOH, 36 ml distilled water, and 9 ml concentrated H_2SO_4; the anolyte a solution of 9 ml concentrated H_2SO_4 in 66 ml distilled water. The temperature was maintained at 50°–55°C throughout the course of the reaction. At a reference potential of −1.10 v vs. a S.C.E. the initial current density was 0.0589 amp/cm². After 80 min the current plateaued at a current density of 0.0143 amp/cm². From the area under the current vs. time curve the total number of coulombs passed was calculated as 15,280 coulombs. The catholyte was treated in the same manner as previously described. A yield of 5.05 (84.3%) of the isoindoline was obtained. The current efficiency in this instance was 77.7%.

4,5,6,7-Tetrachloro-2-(2-dimethylaminoethyl)-3-hydroxyphthalimidine (II).—The same experiment was performed at a reference potential of −0.68 v vs. S.C.E. The initial current density was 0.0189 amp/cm². After 70 min the current plateaued at 0.0107 amp/cm². The catholyte was made basic and the precipitate filtered and dried. Yield 4.31 g (66%), m.p. 158°–162°. Recrystallization from aqueous ethanol gave white crystals, m.p. 164°–165° (corr.); anal. found: C, 40.00; H, 3.45; N, 8.01; Cl, 39.15%. $C_{12}H_{12}N_2Cl_4O_2$ requires C, 40.24; H, 3.37; N, 7.82; Cl, 39.60%.

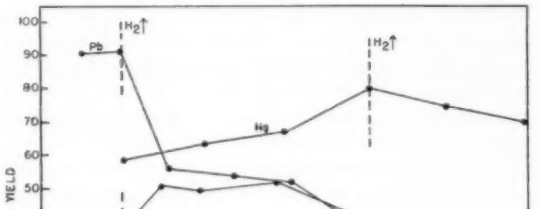


FIG. 2. Dependence of isoindoline yield on current density

DISCUSSION

From results obtained using constant current density it can be seen that with a lead cathode at a current density of 0.0493 amp/cm² the optimum yield and current efficiency is obtained. It is of interest that this is the current density obtained from the calculation of limiting current previously described. A plot of current density vs. yield of isoindoline obtained is shown in Fig. 2.

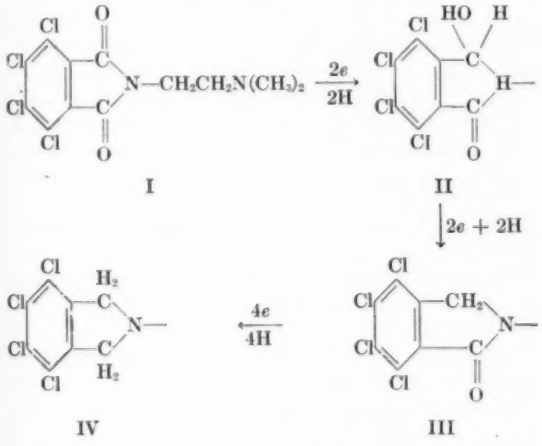
In the experiments with lead and mercury cathodes, the yield of product decreased when the current density was such that gas evolution occurred simultaneously with initiation of electrolysis. This is indicated in Fig. 2 by the current densities to the right of the vertical discontinuous lines. With cadmium the yield of product began to increase beyond the point at which gas evolution was simultaneous with onset of electrolysis and appeared to reach a plateau at 0.07 amp/cm². At this point the amount of gas evolved was moderate as compared to that at 0.048 amp/cm². Beyond the current density at 0.15 amp/cm² the product yield decreased again simultaneously with an increase in gas evolution. One explanation for this phenomena is to associate it with a catalytic effect in which the atomic hydrogen adsorbed on cadmium is a better reducing agent than atomic hydrogen adsorbed on lead or mercury. At the current densities which gave higher yields, conditions were such as to create this state at the electrode surface which enabled the depolarizer to be reduced more effectively than that prior to hydrogen evolution. Beyond the current density of 0.15 amp/cm² the amount of adsorbed hydrogen decreased, as indicated by a greater amount of gas evolution, resulting in a lower reduction efficiency.

The lead cathode may also exert such an effect as indicated by the higher yield of isoindoline obtainable with this electrode whose potential vs. S.C.E. in the aqueous CH_3COOH-H_2SO_4 medium containing the tetrachlorophthalimide appears to be lower than that of the mercury cathode at the current density which gave the maximum yield of isoindoline. Here, however, although difficult to distinguish one from the other, there may be a combination of

an overpotential effect plus a catalytic effect. As the current density is increased to the point at which the catalytic effect is brought to the foreground, the yields obtained parallel those observed at the cadmium electrode. With mercury one obtains a straightforward overpotential effect. The yield increases until the current density is reached at which the maximum effective reference potential vs. S.C.E. is obtained. Beyond that gas evolution takes place with consequent lower yields.

A comparison of the current efficiency obtained when the electrolysis was performed at a lead electrode under the optimum constant current density conditions and under controlled potential conditions shows that, with the former, the current efficiency is considerably lower (45.6%) than the 77.7% efficiency obtained using controlled potential. Thus, from these results, it is obvious that, even in instances wherein controlled potential electrolysis is not absolutely essential in directing the reaction path, providing the electrode is of proper potential to accomplish the reaction, it is important from the standpoint of the limiting current to be used which is dependent on the amount of unreacted depolarizer in the electrolysis medium.

From the products isolated the following may be considered to be the reaction path.



The fact that the hydroxyphthalimidine (II) was obtained at a lower potential than that required for reduction to the isoindoline is to be expected. A previous report (8) has shown that phthalimide can be reduced to hydroxyphthalimidine at a copper electrode. Use of a higher potential electrode, such as lead, resulted in reduction to phthalimidine which, in turn, could be further reduced to isoindoline (9). Reduction of both carbonyl groups does not appear to take place simultaneously for, if the reduction is allowed to proceed for approximately 45% of that required for twice theory for reduction of the tetrachlorophthalimide to the respective isoindoline, the major component isolated is the 4,5,6,7-tetrachloro-2-(2-dimethylaminoethyl)-phthalimidine (III) (78% of theory) with the balance of the isolated material being 4,5,6,7-tetrachloro-2-(2-dimethylaminoethyl)-isoindoline (IV) (10% of theory).

Conclusions

The efficiency of a high overpotential electrode for the reduction of a substituted phthalimide can be increased by utilizing a medium which will raise the overpotential of the electrode and also completely solubilize the depolarizer. This has been accomplished here by using an aqueous-CH_3COOH-H_2SO_4 medium.

It has been demonstrated that the reduction efficiency can be improved considerably by utilizing controlled potential electrolysis in preference to constant current density electrolysis. This can be attributed to the fact that essentially all the current is used for the reduction of the depolarizer, whereas under constant current density conditions, as the concentration of depolarizer diminishes, the excess current is used for the production of hydrogen gas.

The reduction of both carbonyl groups does not occur simultaneously but in a stepwise manner, with the hydroxyphthalimidine being intermediate to the formation of the phthalimidine.

Lead, although a lower potential electrode under the authors' experimental conditions than mercury, appears to exert some catalytic effect on the reduction process with resultant higher product yield and current efficiency.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1957 Journal.

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Polarographic Studies in Acetonitrile and Dimethylformamide

III. Behavior of Quinones and Hydroquinones

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ABSTRACT

Quinones were found to reduce stepwise to the semiquinones and hydroquinone dianions in anhydrous dimethylformamide and acetonitrile at the dropping mercury electrode. Evidence for this behavior was the shift in the second wave brought about by the presence of water and benzoic acid and the electrolytic reductive alkylation of one example, anthraquinone, by ethyl bromide to the diethyl ether of the hydroquinone. Hydroquinones are not oxidized at the dropping mercury electrode in anhydrous acetonitrile or dimethylformamide.

Work on the polarographic behavior of aromatic olefins and hydrocarbons in dimethylformamide and acetonitrile (1) has indicated that these solvents are suitable for studies of organic compounds. Studies have now been carried out with quinones and hydroquinones, examples of reversible organic systems. As in the previous work (1) the results in dimethylformamide were quite similar to those obtained in acetonitrile and will be dealt with together.

Experimental

Polarograms were obtained in a manner similar to that described previously (1). Characteristics for the various dropping mercury electrode used at 60 cm pressure for an open circuit are given in the various tables.

The solvents and supporting electrolytes were purified and prepared according to the directions mentioned earlier (1). The quinones and hydroquinones used were either obtained from stock or prepared according to directions given in the literature.

Electrolyses were carried out in a cell similar to that mentioned in the work on the reduction of hydrocarbons (1). No attempt was made to analyze the gases given off since it was assumed that the same volatile products would be obtained.

Electrolysis of anthraquinone alone.—A suspension of anthraquinone (5.0 g) in acetonitrile (250 ml), which was 0.156*M* in tetrabutylammonium bromide, was electrolyzed using a stirred mercury cathode and a platinum anode. A current starting at 0.58 amp was passed through the solution for 19 hr. The current at the end of this period was 0.10 amp. The color of the catholyte containing the suspended anthraquinone became magenta. As the electrolysis continued long finger-like yellow crystals of anthraquinone appeared on the sintered glass disk in the anode compartment; yield 3.6 g. No reduction products were identified in the solution. The hydroquinone dianion formed had apparently migrated to the anode compartment and had been oxidized either by the bromine liberated, or at the anode to anthraquinone.

With ethyl bromide present during electrolysis.—Anthraquinone (5.0 g) and ethyl bromide (13.5 g) were electrolyzed in acetonitrile (300 ml) which was 0.175*M* in tetrabutylammonium bromide. The current starting at 0.7 amp and ending at 0.15 amp was passed through for 4 hr. The color and formation of anthraquinone needles occurred as in the previous example. The anthraquinone (3.2 g) was removed by filtration. The solution upon removal of the solvent gave a brown residue (22.3 g). Fractional crystallization from ethyl acetate gave tetrabutylammonium bromide (12.0 g) and the very soluble 9,10-diethoxyanthracene. Crystallization of the latter from ethanol gave a sample (1.3 g) melting at 143°–44° which was identified by comparison with an authentic sample (2).

With ethyl bromide added after electrolysis.—Anthraquinone (5.0 g) was electrolyzed in a solution of acetonitrile (180 ml) which was 0.26*M* in tetrabutylammonium bromide using a current of 1.3 amp. After 30 min the current was shut off and ethyl bromide (15.0 g) was added to the magenta colored catholyte and the resulting solution stirred for 2 hr. The unreacted anthraquinone (1.8 g) was filtered and the solvent removed from the resulting solution. The residue was dissolved in a small amount of ethanol and added to a large excess of water. Extraction with ether gave 9,10-diethoxyanthracene (0.3 g).

Electrolysis of benzoquinone.—Using a stirred mercury pool anode and cathode, a solution of benzoquinone (4.5 g) in acetonitrile (200 ml), which was 0.18*M* in tetrabutylammonium bromide, gave after electrolysis for 5 hr considerable tar in both compartments. Removal of the solvent gave a residue from which a trace of hydroquinone was sublimed by heating at 190° under reduced pressure (1 mm).

Reaction of potassium triiodide with 2-methyl-1,4-naphthohydroquinone.—A solution (20 ml) of 0.002*M* 2-methyl-1,4-naphthohydroquinone in acetonitrile when added to 25 ml of 0.001*M* KI_3 in acetonitrile did not decolorize the latter after a period of 8 hr. The addition of water (3 ml) to such a mixture (20 ml) caused decolorization in 6 min. Use of equal volumes of water and mixture caused immediate decolorization.

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TABLE I. *Half-wave potentials, diffusion currents and diffusion current constants for various compounds in solutions containing 0.1M tetrabutylammonium bromide*

Quinone	Concn. millimoles/liter	i_d, 1st wave	i_d, 2nd wave	I_d[a] 1st wave	I_d[a] 2nd wave	E1/2(v) vs. Hg pool 1st wave	E1/2(v) vs. Hg pool 2nd wave	0.059/n[b] 1st wave	0.059/n[b] 2nd wave
Acetonitrile									
Benzoquinone[d]	1.00	4.67	3.58	3.07	2.35	−0.10[c]	−0.84	[c]	0.081
Duroquinone[d]	1.00	5.37	3.98	3.53	2.62	−0.33	−1.05	0.036	0.086
2-Methyl-1,4-naphthoquinone[d]	1.00	5.07	4.08	3.33	2.68	−0.27	−0.94	0.049	0.039
Anthraquinone[d]	1.00	4.97	3.78	3.27	2.49	−0.43	−1.05	0.050	0.048
Ethyl bromide[e]	4.86	52.7		6.35		−2.13			
Dimethylformamide									
Benzoquinone[e]	0.938	[c]	2.64	[c]	1.59	[c]	−0.92	[c]	0.107
2-Methyl-1,4-naphthoquinone[e]	1.15	4.34	3.46	2.14	1.70	−0.20	−1.02	0.085	0.093
2-Methyl-1,4-naphthoquinone[f, g]	1.12	4.07	4.05	2.12	2.10	−0.34	−1.05	0.083	0.125
Anthraquinone[e]	1.45	5.44	4.56	2.12	1.78	−0.34	−1.10	0.073	0.077
2-Methyl-1,4-naphthohydroquinone	No oxidation								
Hydroquinone	No oxidation								

[a] $I_d = \dfrac{i_d}{C m^{2/3} t^{1/6}}$.

[b] From current-voltage curve analysis.
[c] Maximum.
[d] Capillary with $m^{2/3}t^{1/6}$ of 1.52 $mg^{2/3}sec^{-1/2}$ and a droptime of 4.7 sec.
[e] Capillary with $m^{2/3}t^{1/6}$ of 1.77 $mg^{2/3}sec^{-1/2}$ and a droptime of 3.96 sec.
[f] Inert electrolyte, 0.1*M* $NaNO_3$.
[g] Capillary with $m^{2/3}t^{1/6}$ of 1.71 $mg^{2/3}sec^{-1/2}$ and a droptime of 4.28 sec.

TABLE II. *Effect of water and benzoic acid on the polarographic behavior of various quinones in solutions containing 0.1M tetrabutylammonium bromide*

Quinone	% Water by volume	i_d 1st wave	i_d 2nd wave	E1/2 (v) vs. Hg pool 1st wave	E1/2 (v) vs. Hg pool 2nd wave	0.059/n[a] 1st wave	0.059/n[a] 2nd wave
Acetonitrile							
Duroquinone[b]	0.5	5.27	3.98	−0.34	−0.76	0.115	0.075
	1.0	5.37	3.98	−0.33	−0.67	0.050	0.107
	2.44	5.57	3.78	−0.35	−0.62	0.051	0.097
	4.76	9.05	—	−0.39	—	0.115	—
2-Methyl-1,4-naphthoquinone[b]	1.0	4.97	3.78	−0.27	−0.66	0.060	0.079
	2.44	5.17	3.68	−0.29	−0.57	0.069	0.063
	4.76	4.97	3.78	−0.30	−0.50	0.049	0.071
Anthraquinone[b]	0.5	4.97	3.88	−0.45	−0.89	0.055	0.060
	1.0	4.97	3.78	−0.45	−0.83	0.035	0.063
	4.76	4.77	3.98	−0.48	−0.71	0.043	0.061
	20.0	8.05	—	−0.58	—	0.089	—
Benzoquinone[b]	1.0	4.67	3.28	−0.09[c]	−0.46	[c]	0.062
	4.76	4.27	2.78	−0.06	−0.28	0.020	0.049
Dimethylformamide							
Anthraquinone[d] and benzoic acid[e]	0	7.13	—	−0.33	—	0.069	—

[a] From current-voltage curve analysis.
[b] Concentration, 0.001*M*. Capillary with $m^{2/3}t^{1/6}$ of 1.52 $mg^{2/3}sec^{-1/2}$ and a droptime of 4.7 sec.
[c] Maximum interferes.
[d] Concentration 0.00106*M*. Capillary with $m^{2/3}t^{1/6}$ of 1.77 $mg^{2/3}sec^{-1/2}$ and a droptime of 3.96 sec.
[e] Concentration 0.0035*M*.

TABLE III. *Effect of water on the polarographic oxidation of 2-methyl-1,4-naphthohydroquinone in dimethylformamide with 0.1M* $NaNO_3$ *as the inert electrolyte*

Conc. millimoles/liter	% H_2O by volume	id/C[a]	E1/2 (v) vs. Hg pool	0.059/n[b]
2.24	0.5	5.09	+0.927	0.120
2.23	1.0	5.11	+0.889	0.103
2.22	1.48	5.00	+0.838	0.089
2.21	1.96	4.98	+0.863	0.062
3.20	1.96	4.94	+0.860	0.105
3.18	2.44	4.84	+0.886	0.110
3.10	4.76	4.71	+0.768	0.081
2.83	13.04	4.20	+0.671	0.108
2.72	16.66	3.82	+0.617	0.091
2.61	20.00	3.70	+0.543	0.103
2.17	33.33	3.24	+0.403	Max
1.86	42.86	2.96	+0.380	Max

[a] Capillary with $m^{2/3}t^{1/6}$ of 1.71 $mg^{2/3}sec^{-1/2}$ and a droptime of 4.28 sec.
[b] From current-voltage curve analysis.

Results

The polarographic data obtained for the various quinones are shown in Table I. The waves in all cases were well defined except for benzoquinone; a maximum was obtained for the first wave which could not be suppressed. To study the effect of acids on the reduction, the polarographic behavior of the quinones was studied in the presence of water and benzoic acid and is given in Table II.

The behavior of 2-methyl-1,4-naphthohydroquinone in acetonitrile and in dimethylformamide in the presence of various amounts of water is given in Tables III and IV.

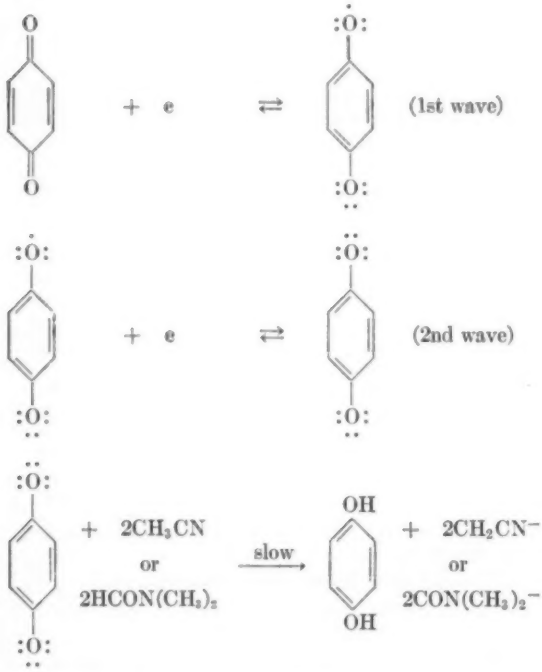
TABLE IV. *Effect of water on the polarographic oxidation of 2-methyl-1,4-naphthohydroquinone in acetonitrile with 0.1M* $LiClO_4$ *as the inert electrolyte*

Conc. millimoles/liter	% H_2O by volume	id/C[a]	$E_{1/2}$(v)[b]
1.25	0.0	No wave	No wave
1.24	0.5	No wave	No wave
1.23	1.48	8.70	+0.713
1.21	2.91	8.06	+0.623
1.19	4.76	7.53	+0.095
1.00	20.00	7.09	+0.062
0.83	33.33	6.80	+0.0620
0.71	42.86	6.39	+0.022

[a] Capillary with $m^{2/3}t^{1/6}$ of 1.62 $mg^{2/3}sec^{-1/2}$ and a drop-time of 5.13 sec.
[b] Slight maximum present.

Discussion of Results

Examination of data in Table I indicates that the reduction of quinones at the dropping mercury electrode in anhydrous acetonitrile and dimethylformamide proceeds first to the semiquinone and then to the hydroquinone dianion. The reactions involved are illustrated with benzoquinone:



Analyses of the current-voltage curves were not consistent but approximated a one-electron change in a number of the examples and are in agreement with these steps.

Addition of water has no effect on the first wave (Table II) but causes the second wave to shift to more positive potentials. In the presence of a large amount of water the two waves merge and give a single wave approximately equal in height to the sum of the two waves obtained in anhydrous media. Benzoic acid being a stronger acid than water is effective at a much lower concentration in causing this shift to take place.

Since only the second wave is affected under these conditions, the following reactions are involved using the notation Q for quinone and S for the semiquinone or Q^-:

$$Q + e \rightleftarrows S$$
$$S + e \rightleftarrows Q^{--}$$
$$Q^{--} + 2H^+ \rightleftarrows QH_2 \text{ fast}$$

The potential of the dropping mercury at any point on the second wave should be given by

$$E_{d.e} = E^0 - \frac{RT}{n\mathbf{F}} \ln \frac{[Q^-]}{[S]}$$

Since the reaction of the quinone dianion with acid (or water) is rapid then Q^- can be replaced by

$$Q^- = \frac{K[QH_2]}{[H^+]^2}$$

where K is the dissociation constant for the hydroquinone in the solvent involved. The first equation then becomes

$$E_{d.e} = E^0 - \frac{RT}{\mathbf{F}} \ln K \frac{[QH_2]}{[S]} + \frac{RT}{\mathbf{F}} \ln [H^+]^2$$

Addition of acid (or water) should shift the wave to more positive potentials and experimentally this phenomenon is observed.

This shift of the second wave with increasing acidity could also be explained by a relatively slow reaction between the

$$Q^- + H^+ \rightleftarrows QH^-$$

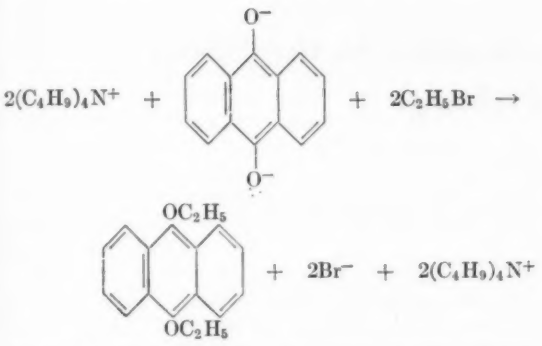
hydroquinone dianion and the acid since the surface concentration of Q^- would decrease with increasing H^+. The first mechanism could be distinguished from this slow reaction since it predicts a quantitative shift with a change in H^+ concentration. Unfortunately not enough data were available to test this relationship.

The formation of dianions as the final products is substantiated by observations made during the polarographic reduction of anthraquinone and by the products isolated in the large-scale reduction of anthraquinone. In the former a red color has been observed surrounding the mercury drop. This phenomenon has also been reported by others (3). The coloration is similar to that observed when anthrahydroquinone is dissolved in aqueous alkali in the absence of air.

In the large-scale electrolytic reduction of anthraquinone the reduction product migrates to the anode compartment and is reoxidized to anthraquinone which crystallizes on the sintered glass disk separating the two compartments. The intermediate dianion persists even after the current is turned off since treatment of a solution, which had been electrolyzed for 30 min with a current of 1.3 amp, with ethyl bromide gave a 6% yield of 9,10-diethoxyanthracene.

Electrolysis when carried out in the presence of ethyl bromide for 4 hr with an average current of 0.5 amp, gave a 20% yield of the diether.

The reaction of the quinone dianion is very slow with



the anhydrous solvents since the yields of hydroquinone in electrolytic preparations were very low. The source of the protons is the same, however, as indicated for the reduction of unsaturated hydrocarbons (1).

The diffusion-current constants (I) for the two waves differ in each of the solvents studied; the second wave height is approximately 0.8 of that of the first wave. The reason for this difference is not known, but several explanations offer themselves.

The higher first wave may be caused by the disproportionation reaction reported to occur with semiquinones. The effective

$$2S + Q + Q^{=}$$

concentration of quinone would then become magnified by this step.

A second possibility involves the behavior of the semiquinone during the formation of the second wave. The semiquinone is negatively charged and could be repelled from the diffusion layer around the cathode into the bulk of the solution. The supporting electrolyte would not prevent this migration since only positive ions of the latter are in the vicinity of the cathode. This explanation is favored over the first since the ratio of wave heights is approximately the same for all of the quinones. If disproportionation were involved, the amount would be expected to vary with structure.

The oxidation of hydroquinone and of 2-methyl-1,4-naphthohydroquinone did not occur in anhydrous dimethylformamide or acetonitrile. Addition of water to the latter, as shown in Table III and IV, gave only one wave which shifted to more negative potentials with increasing amounts of water. The resistance of the hydroquinones to oxidation under these conditions indicates that ionization of the hydroquinones is a prerequisite for the oxidation of these compounds. Dimethylformamide and acetonitrile with dielectric constant of about 35 are poorer ionizing solvents than water and are responsible for this behavior. This property has been verified chemically by a study of the oxidation of 2-methyl-1,4-naphthohydroquinone by the triiodide ion. A solution of the two in anhydrous acetonitrile was stable for 8 hr. Addition of water accelerated the reaction; the use of a 15% water gave a reaction in 6 min.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1957 JOURNAL.

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Mechanism of Ozone Formation in the Silent Electric Discharge

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ABSTRACT

The kinetics of ozone formation from oxygen have been studied in a Siemens ozonizer. Measurements were made at pressures from 70 to 400 mm and temperatures from −30° to −100°C. The results suggest that oxygen atoms, produced in the discharge, both form ozone by three body collisions with oxygen molecules and also destroy it, leading to a steady-state ozone concentration at sufficiently long residence times. The ratio of rate constants for these two reactions, and their activation energy difference, are similar to those found by Eucken and Patat in the photolysis of oxygen. At the higher temperatures, thermal ozone decomposition becomes an important factor in determining the steady-state ozone concentration. The variation of steady-state ozone concentration with pressure suggests that the combination of oxygen atoms and molecules to form ozone changes from termolecular to bimolecular in the pressure range investigated. The lifetime of the activated ozone complex, thus measured, is of the expected order of magnitude for the number of vibrational degrees of freedom involved. The possible role of other ozone destruction reactions is also considered.

Ozone is formed by the interaction of ionizing radiations with oxygen as well as by most types of gas discharges in oxygen (1, 2). A steady-state ozone concentration is attained, the value of which depends largely upon the system used. In general, it increases with increasing pressure and decreasing temperature, and in some cases is dependent upon the nature of the containing walls.

In a low temperature discharge plasma, the energy leading to chemical reaction is transferred to molecules by the faster electrons on the tail of an energy distribution approximating Maxwellian, to produce electronically excited states and ions. Assume as a first hypothesis that the ions, if they contribute appreciably to the over-all reaction, do so after neutralization, leading to electronically excited molecules and atoms (3). The excited molecules and atoms may then undergo reactions in a manner similar to that in which they occur in photochemical systems. It is the purpose of this work to study the kinetics of oxygen decomposition in the discharge, and to compare them with those of the photolytic reaction, in an effort to determine the validity of this hypothesis.

The limiting quantum yield, ϕ, for ozone formation at small conversions has been found to be about 2 over the wave-length range from 1295 to 2070Å (4), strongly suggesting the reactions:

$$O_2 + h\nu \xrightarrow{I_a} 2\,O \qquad (a\text{-}1)$$

$$O + O_2(+M) \xrightarrow{k_2} O_3(+M) \qquad (b)$$

Eucken and Patat (5) have studied the photolysis of oxygen in a flow system and have found the simple sequence of reactions (a-1) and (b), together with (c), to be compatible with their data over the pressure range from 13 to 40 mm.

$$O + O_3 \xrightarrow{k_3} 2\,O_2 \qquad (c)$$

Assuming the third body in reaction (b) to be an oxygen molecule, this leads to the expression:

$$\frac{d[O_3]}{dt} = \phi I_a \left\{\frac{1 - \alpha[O_3]}{1 + \alpha[O_3]}\right\} \qquad (I)$$

where

$$\alpha = \frac{k_3}{k_2[O_2]^2}$$

It is readily seen that the steady-state ozone concentration is equal to $1/\alpha$, and that, in agreement with the data of Eucken and Patat, it is proportional to the square of the pressure,[1] P_{O_2}, and is independent of the light intensity. They evaluated k_3/k_2 and measured the activation energy difference $E_3 - E_2 = 6.16$ kcal.

Experimental Method

The reaction rate was measured in a conventional Pyrex flow system. Commercial oxygen was dried by passing through a trap at −78°C, the trap containing glass wool and stainless steel helices to improve heat transfer. An aneroid-type manometer was used so that the system was free of mercury vapor. The ozonizer was of the Siemens type, with two concentric Pyrex cylinders serving as dielectrics. The outer electrode was aluminum foil 8 cm in length, with a diameter of 2 cm. The inner electrode con-

[1] Actually, the product of total pressure and oxygen pressure together with a factor defining the relative efficiencies of ozone and oxygen as third bodies for reaction (b) should appear in equation (I). Since, however, except at low temperatures, the maximum ozone concentration found in the author's investigation amounted to less than 4 volume % with a change over the complete pressure range of less than 2 volume %, the author will neglect these factors as did Eucken and Patat, and use the total measured pressure as the partial pressure of oxygen.

sisted of an aquadag coating, electrical connection being made through a small amount of mercury. The gap containing oxygen was 2 mm and the Pyrex dielectrics were each 1 mm thick. The voltage to the ozonizer was obtained from a 12,000-v ignition transformer with a Variac in the primary. The current was measured in the ground circuit with a copper oxide rectifier-type 0 to 1 ma meter, bypassed with a 0.1 μf condenser. The current below onset of the discharge was essentially zero, and rose abruptly as the discharge started.

The ozone concentration in the effluent was determined by measuring absorption of 2537Å radiation from a 4-watt G.E. germicidal lamp in a quartz cell 2.5 cm in diameter and 1 cm in depth (6). The radiation was collimated and was measured on an FJ405 photoelectric cell. The system was calibrated by passing various O_2-O_3 mixtures through the cell and a calibrated volume in series until the composition in the two was the same. The ozone in the bulb was absorbed by shaking in contact with 15 ml of 2N neutral KI, and the liberated I_2 was titrated with standard thiosulfate.

Preliminary results indicated that, at the very low flow rates used in determining steady-state ozone concentrations, a considerable error was introduced owing to ozone photolysis in the measuring cell. To obviate this difficulty, a shutter was placed between the cell and the lamp, and the photoelectric current was measured on a G.E. photoelectric potentiometer recorder. The ozone concentration could then readily be determined by extrapolation to zero time after the shutter was opened. This method was used for all the experiments reported in this paper.

Results

Comparison with the Simple Mechanism

If reaction (a-1) is replaced with the reaction corresponding to electron impact,

$$O_2 + e \xrightarrow{k_1} 2\,O + e \qquad (a\text{-}2)$$

equation (I) remains the same except that ϕI_a is replaced by k_1, where k_1 is defined for reaction (a-2) by the relation

$$\frac{d[O]}{dt} = k_1$$

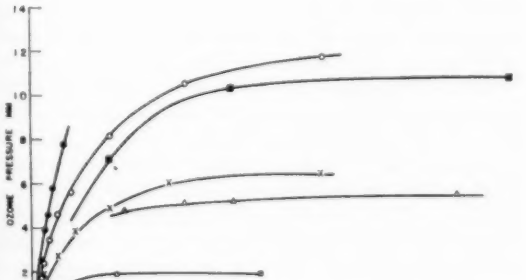

FIG. 1. Partial pressure of ozone as a function of residence time in the discharge at various total pressures. + 69 mm; □ 100 mm; △ 176 mm; × 200 mm; ■ 274 mm; ○ 301 mm; ● 500 mm.

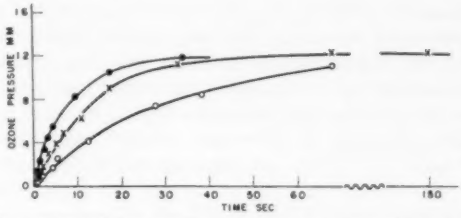

FIG. 2. Partial pressure of ozone as a function of residence time in the discharge at various currents. ○ 0.06 ma; × 0.14 ma; ● 0.30 ma.

TABLE I. *Variation of steady-state ozone pressure with total pressure at 25° and 59.2°C*

Current, 0.30 ma

Temp	P_{O_2}	P'_{O_3}	$P^2_{O_2}/P'_{O_3}$
°C	mm	mm	mm × 10^{-3}
25	69	0.92	5.16
25	100	1.92	5.21
25	176	5.26	5.91
25	200	6.41	6.24
25	274	10.5	7.18
25	301	11.9	7.63
59.2	100	0.97	10.3
59.2	150	2.12	10.6
59.2	200	3.44	11.6
59.2	301	7.02	12.9
59.2	350	8.47	14.5
59.2	399	10.7	15.0

The quantity k_1 will be a function of the current, average electron energy, pressure, and composition of the gas. The nature of k_1 needs no further consideration at this point, since, for the simple mechanism above the steady state ozone concentration is independent of k_1 (equation I).

Variation in ozone partial pressure with residence time in the ozonizer at various total pressures is shown in Fig. 1. The current was 0.30 ma, and the ambient temperature 25°C. Values of the steady-state ozone pressure, P'_{O_3}, obtained from these and similar curves obtained at 59.2°C, together with values of $P^2_{O_2}/P'_{O_3}$, are shown in Table I. While at lower pressures $P^2_{O_2}/P'_{O_3}$ approaches a constant value [as required by equation (I)], very definite departures occur at higher pressures.

Fig. 2 shows the dependence of rate of ozone formation on discharge current. These results were obtained at 301 mm pressure with an ambient temperature of 25°C. As predicted by the simple mechanism, the steady-state ozone concentration is independent of discharge current.

Perhaps the simplest assumption one might make to account for the increase in $P^2_{O_2}/P'_{O_3}$ at higher P'_{O_3} involves decomposition of the ozone by some process in addition to that of reaction (c), as, for example, by electron impact. Thus, if $P^2_{O_2}/P'_{O_3}$ is plotted against P'_{O_3} and extrapolated to $P'_{O_3} = 0$, the value of k_3/k_2 [2] should be obtained. Further

[2] The quantity k_2/k_3 in equation (I) is expressed in concentration units. Since the authors, like Eucken and Patat, have expressed their results in units of pressure, the intercept in Fig. 3 gives k'_3/k'_2 mm, where $k'_3/k'_2 = (k_3/k_2)\cdot RT$. Eucken and Patat do not appear to have made this distinction, which is of importance in evaluating the activation energies. In a similar manner, k'_1 is defined in terms of pressure as $k_1\,RT$ mm.

implications of this mechanism will be considered shortly; but, assuming its validity, the value of k_2'/k_3' may be compared with that of Eucken and Patat. The data of Table I are plotted in Fig. 3, from which it is evident that a reasonable extrapolation can be made. Values of k_2'/k_3' thus obtained are 2.08×10^{-4} mm^{-1} at 25°C and 1.02×10^{-4} mm^{-1} at 59.2°C. Eucken and Patat give 5.35×10^{-4} mm^{-1} at 25°C and 1.91×10^{-4} mm^{-1} at 59.2°C. Exact comparison of these values is difficult, since the temperature of the gas in the ozonizer is probably somewhat higher than that of its surroundings. From other measurements (10) of discharge temperatures, the required temperature rise is completely reasonable, although it should be noted in Fig. 2 that no variation in P'_{O_2} occurred with changing discharge current, where a change in temperature might have been anticipated. In any event, the agreement seems fairly satisfactory and indicative of the similarity of mechanisms.

Decomposition of Ozone by Electron Impact

Including the electron decomposition reaction

$$O_3 + e \xrightarrow{k_4} O_2 + O + e \qquad (d)$$

in the simple mechanism above, one has

$$\frac{d[O_3]}{dt} = k_1 \left\{\frac{1 - \alpha[O_3]}{1 + \alpha[O_3]}\right\} - \frac{2\alpha k_4[O_3]^2}{1 + \alpha[O_3]} \qquad (II)$$

which leads to equation (I) at small ozone concentrations. Under steady-state conditions, this gives

$$\frac{[O_2]^2}{[O_3]_{ss}} = k_3/k_2(1 + 2\,k_4/k_1[O_3]_{ss}) \qquad (III)$$

Here $[O_3]_{ss}$ refers to the steady-state ozone concentration.

A comparison of equation (III) with the results in Fig. 2 and 3 indicates that, if this mechanism is correct, k_4/k_1 must be independent of pressure and discharge current. To establish these dependences, it is now necessary to examine the factors controlling these rate constants in more detail.

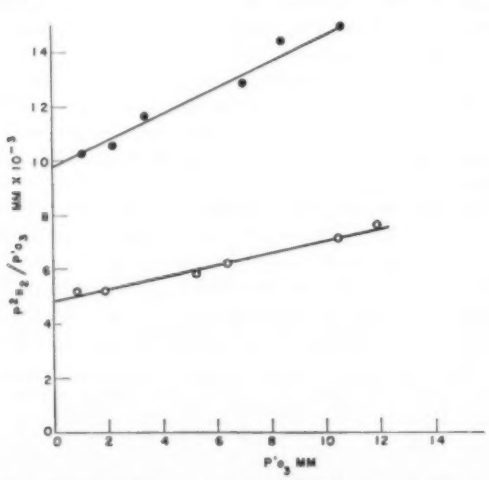

FIG. 3. Dependence of ratio $P^2_{O_2}/P'_{O_3}$ on steady-state partial pressure of ozone. ○ 25°C; ● 59.2°C.

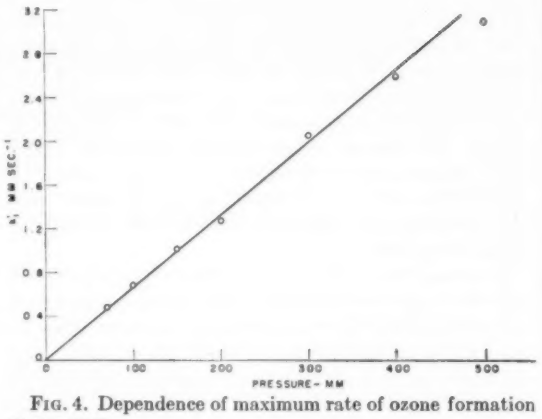

FIG. 4. Dependence of maximum rate of ozone formation on pressure.

The rate of any specified type of electron collision process in a uniform plasma is given by the expression (7)

$$R_x = k\,\frac{i[X]}{W}\int_{V_e}^{\infty} Q(V)\cdot f(V)\,dV \qquad (IV)$$

where i is the current density; $[X]$ is the concentration of the component undergoing collision; W is the electron drift velocity; $Q(V)$ is the probability cross section for the specified type of collision process; $f(V)\,d(V)$ is the probability that an electron has energy lying between V and $V + dV$; k is a constant for all such processes; and V_e is the critical potential for the specified process.

While in the silent electric discharge the plasma may not be uniform, it is to be expected that an expression similar to that above may be obtained by averaging over the discharge volume and time. The quantity W and the integral in equation (IV) are functions of E/P, where E is the field strength and P the pressure, so that one may write[3]

$$2\,\frac{k_4}{k_1} = \frac{1}{[O_2]}\,\frac{I_4}{I_1} \qquad (V)$$

where I_4 and I_1 refer to the integrals in equation (IV) for the case of electron collision with ozone and oxygen, respectively. Here we have assumed that each inelastic collision of the type given by equation (IV) leads to reactions (a-2) or (d). If more than one excited state can lead to reactions (a-2) or (d), the integrals in equation (V) must be replaced by a corresponding summation of integrals.

Since k_1' is measured directly by the initial slopes of the curves in Fig. 1, its dependence on pressure, and thus that of I_1/W, can be determined. Values of k_1' as a function of pressure are plotted in Fig. 4, where it is seen that a linear relation holds. In obtaining the initial slopes, greatly expanded scales were used, and in all cases good initial straight lines were obtained at the fast flow rates used. The discharge current was 0.30 ma and the temperature was 25°C. Comparing these results with equation (IV) indicates that with pressures from 70 to 500 mm, I_1/W and thus the electron energy distribution is relatively con-

[3] In deriving equations (II) and (III), the rates of production of oxygen atoms by reactions (a-2) and (d) have been assumed to be k_1 and $k_4\,[O_3]$, respectively.

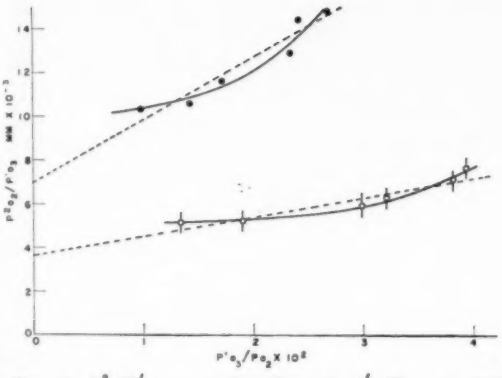

FIG. 5. $P^2_{O_3}/P'_{O_3}$ as a function of P'_{O_3}/P_{O_2}. ○ 25°C; ● 59.2°C.

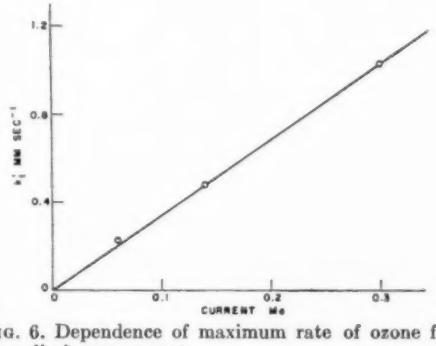

FIG. 6. Dependence of maximum rate of ozone formation on discharge current.

stant over the energy range of interest. These results are consistent with Manley's (8) observation that in the ozonizer discharge E/P is independent of pressure over the range of 1–2 atm for gaps of the order of magnitude used in this work. While some variation is to be expected, particularly at lower pressures, it is apparently insufficient to change I_1/W appreciably. It may then be expected that the ratio of I_4/I_1 appearing in equation (V) will be a constant independent of pressure.

Combining equations (V) and (III), it is apparent that the slope of the curve in Fig. 3 should not be a constant but should decrease as $1/P_{O_2}$, i.e., by a factor of about 4. For comparison with Fig. 3, $P^2_{O_3}/P'_{O_3}$ is plotted against P'_{O_3}/P_{O_2} in Fig. 5. It is evident that, while the individual points do not lie far from the dashed straight lines drawn, there is a definite trend from linearity. The data suggest, although perhaps not conclusively, that electron collision with ozone is not an important destructive step over the concentration range encountered in this work.

Equation (IV) predicts that both k_1 and k_4 should be proportional to the discharge current. Fig. 6 shows that this is indeed true for k'_1. Thus, equation (III) does predict that the steady-state ozone concentration should be independent of discharge current as was shown in Fig. 2.

Third Body Restrictions in Ozone Formation

To this point it has been assumed that reaction (*b*), the combination of oxygen atoms with oxygen molecules to form ozone, is second order in oxygen concentration, since stabilization by collision with a third body is necessary. At sufficiently high pressures all active complexes will be stabilized by collision and the reaction rate will become first order in oxygen concentration. This is similar to the order change postulated by Lindemann for unimolecular reactions, and becomes clear when reaction (*b*) is represented by the following steps.

$$O + O_2 \underset{\kappa_3}{\overset{\kappa_2}{\rightleftharpoons}} O_3^* \qquad (e)$$

$$O_3^* + O_2 \xrightarrow{\kappa_4} O_3 + O_2 \qquad (f)$$

Here O_3^* refers to the activated complex containing an amount of energy approximately equal to $D(O - O_2)$, or 25 kcal.

Solving the kinetics for this situation including reactions (*a*-2) and (*c*), and assuming a steady state in [O] and $[O_3^*]$, one finds:

$$\frac{d[O_3]}{dt} = \frac{k_1(1 - \gamma[O_3])}{1 + \gamma[O_3]} \qquad (VI)$$

an equation analogous to that obtained with the simple mechanism of equation (I), except that now

$$\gamma = \frac{k_3(\kappa_3 + \kappa_4[O_2])}{\kappa_4\kappa_2[O_2]^2} \qquad (VII)$$

Since, as before, $\gamma = 1/[O_3]_{ss}$ it is evident that at high pressures when the rate of collisional deactivation is large compared with the spontaneous decomposition of O_3^* (i.e., $\kappa_4[O_2] \gg \kappa_3$), $[O_3]_{ss} \propto [O_2]$; whereas at low pressures (when $\kappa_3 \gg \kappa_4[O_2]$), $[O_3]_{ss} \propto [O_2]^2$.

Equation (VII) may be written:

$$\frac{[O_2]^2}{[O_3]_{ss}} = \frac{k_3(\kappa_3 + \kappa_4[O_2])}{\kappa_4\kappa_2} \qquad (VIII)$$

As Fig. 7 indicates, the data taken from Table I are consistent with equation (VIII) if all of the rate constants are essentially pressure independent. While theory and experiment have indicated that for unimolecular decompositions of the type shown in (III) κ_3 will be somewhat pressure dependent, as has already been noted in the preceding section, the data shown in Fig. 7 are not sufficiently accurate to clearly show the expected variations. Thus, rate constants evaluated from Fig. 7 will be averages for the pressure range shown. From the ratios of intercepts to slopes $(\kappa_3/\kappa_4)_{298} = 2.00 \times 10^{-2}$ mole liter^{-1} and $(\kappa_3/\kappa_4)_{332} = 2.24 \times 10^{-2}$ mole liter^{-1}, where the subscripts refer to absolute temperature. If one writes $\kappa_4 = f.Z$, where Z is the collision number and f the fraction of collisions between O_2 and O_3^* leading to deactivation, one finds $(\kappa_3)_{298} = 3.31 \times 10^9 f$ sec^{-1} and $(\kappa_3)_{332} = 3.77 \times 10^9 f$ sec^{-1}. Here for the sum of the collision radii O_2 and O_3^* a value of 4Å has been used.

Comparison may be made with the mean value of κ_3 obtained using the approximate expression developed by Benson (9)

$$\kappa_3 = \nu\left[1 + \frac{\epsilon^*}{(n-1)kT}\right]^{1-n} \qquad (IX)$$

Here $\nu \sim 10^{13}$; n is the number of degrees of freedom which

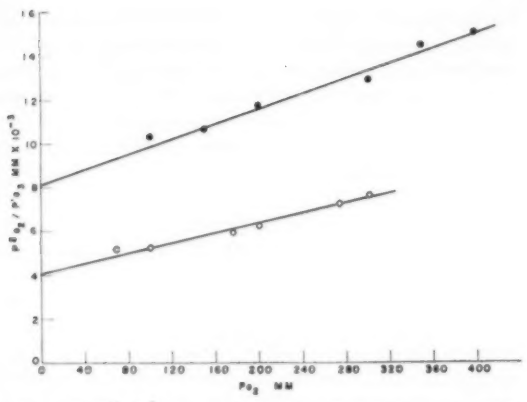

FIG. 7. $P^2_{O_2}/P'_{O_3}$ as a function of pressure. ○ 25°C; ● 59.2°C.

may contribute to reaction, in this case 3; and ϵ^* is the minimum energy for decomposition, in this case 25 kcal. With these values equation (IX) gives $(\kappa_3)_{298} = 2.34 \times 10^{10}$ sec^{-1}, which is to be compared with the measured value of 3.31×10^9 sec^{-1} if $f = 1$. In view of the approximations made in Benson's treatment, this order of magnitude agreement seems reasonable.

Fig. 7 gives somewhat different intercepts for $P^2_{O_2}/P'_{O_3}$ from those obtained using Fig. 3. For purposes of comparison with the results of Eucken and Patat these intercepts give $k'_2/k'_3 = 2.44 \times 10^{-4}$ mm^{-1} at 25°C and 1.22×10^{-4} mm^{-1} at 59.2°C, values in slightly better agreement with those of Eucken and Patat than were obtained using Fig. 3.

Temperature Effects

The dependence of κ_3 on temperature is described by equation (IX). Since for this system $2kT \ll \epsilon^*$ this may be written to a close approximation as

$$\frac{(\kappa_3)_{T_1}}{(\kappa_3)_{T_2}} = \left(\frac{T_1}{T_2}\right)^2 \qquad \text{(X)}$$

From values in the preceding section $(\kappa_3)_{298}/(\kappa_3)_{322} = 0.88$. Equation (X) predicts a value of 0.81, probably fortuitous agreement considering the uncertainty of the discharge temperature and the nature of the calculation.

Assuming this temperature dependence for κ_3 [equation (X)], and that the pre-exponential factors of the remainder of the rate constants involved are proportional to $T^{1/2}$, equation (VIII) may be written

$$\frac{d \ln \phi}{d\ 1/T} = -\frac{[E_3 - E_2]}{R}$$

where (XI)

$$\phi = \frac{1}{T^{5/2}} \cdot \frac{1}{[1 + K \cdot P_{O_2} \cdot T^{-5/2}]} \cdot \frac{P^2_{O_2}}{P'_{O_3}}$$

K is temperature independent, and is evaluated from the slope and intercept of the straight line for 25°C in Fig. 7. E_3 is the activation energy for reaction (c), and E_2 that corresponding to κ_2 [reaction (e)].

Therefore, from measurements of P'_{O_3} at various temperatures, an Arrhenius plot may be constructed according to equation (XI). The results of such measurements are shown in Fig. 8, taken from the data in Table II over a temperature range from −31° to +102°C. Fig. 8 shows that, while below 60°C the curve is linear, above this temperature a large increase in apparent activation energy occurs. This change at higher temperatures is almost certainly associated with the onset of thermal ozone decomposition. The data shown in Fig. 9, where the variation in P_{O_3} with residence time at 102°C is plotted, lend support to this conclusion. Comparison of this curve with those in Fig. 1 shows that, unlike the latter, a true steady state is not reached at the higher temperatures, but rather, at longer residence times increased ozone decomposition occurs. From the linear portion in Fig. 8 one finds $E_3 - E_2 = 3.9$ kcal $mole^{-1}$ $degree^{-1}$.

Since Eucken and Patat assumed $k_3 \propto T^{1/2}$, and used pressure units instead of concentration units for k_3/k_2, a recalculation of $E_3 - E_2$ was made from their data using

TABLE II. *Variation in steady-state partial pressure of ozone with temperature*

Pressure of oxygen = 150 mm; discharge current = 0.30 ma

Temp	P'_{O_3}
°C	*mm*
−31	16.4
0	8.48
25	4.19
41	3.36
59	2.12
84	0.85
102	0.31

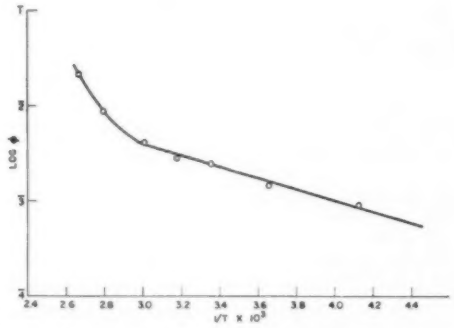

FIG. 8. Arrhenius plot determining activation energy difference $E_3 - E_2$.

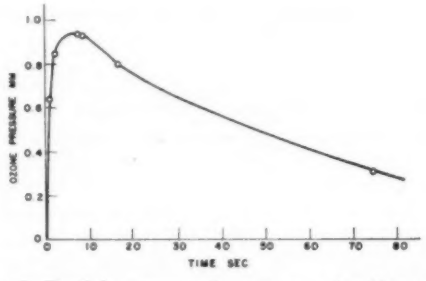

FIG. 9. Partial pressure of ozone as a function of residence time in the discharge at 102°C.

equation (XI), and assuming $K \cdot P_{O_2} \cdot T^{-5/2}$ to be essentially zero. The value of $E_3 - E_2$ obtained was 4.7 kcal mole^{-1} degree^{-1}. Whether the difference between the ΔE of Eucken and Patat and that obtained in this work is significant is not clear. The author's value would be too low if the discharge temperature were higher than ambient. The discrepancy might also be explained by assuming that in the discharge some of the oxygen atoms carry excess energy, either as kinetic energy or because they are in higher electronically excited states.

Discussion

While comparison between the photochemical and discharge data, particularly the general agreement in k_2/k_3 and $E_3 - E_2$, indicates the similarities between the mechanisms, and thus the essential importance of oxygen atoms in the discharge phenomenon, little direct information concerning the primary states leading to formation of atoms has been obtained. Of particular interest is the relative role of ions and electronically excited molecules as precursors to atom formation. It is to be noted, however, that a mechanism involving ozone formation directly from ions, such as that postulated by Brewer and Westhaver (11), is unlikely in view of our results.

The data indicate that at higher pressures than those used by Eucken and Patat the steady-state ozone concentration is lower than would be predicted by their simple mechanism. This has been explained by assuming that the lifetime of the activated ozone complex becomes comparable with the time between deactivating collisions in this higher pressure range, so that the rate of formation of ozone from oxygen atoms becomes proportional to less than the square of the pressure. Such a concept leads to a lifetime for the activated ozone complex of the expected order of magnitude for the number of degrees of freedom involved. While the results of Schumacher and Kistiakowski (12) on the photolysis of ozone fail to show the effect of order change in reaction (*b*) the experimental error claimed would be sufficient to mask the effect using the author's values for k_3 and k_4. Ritchie (13), in a study of the thermal decomposition of ozone, found evidence of a change in order of the initial step from second to first in the pressure range of 10 to 100 mm, suggesting that in this pressure range the lifetime of the thermally activated complex becomes comparable to the collision time. This would be expected to occur at a somewhat lower pressure in this case since the average energy of the activated complexes would be somewhat lower than when they are formed by combination of oxygen atoms with oxygen molecules.

The anomalously low steady-state ozone concentration at higher pressures might also be explained assuming an ozone destruction reaction in addition to reaction (*c*). The possibility that this destruction reaction involves collisions between electrons and ozone molecules according to reaction (*d*) has been discussed and while present results do not conclusively rule it out, they favor a pressure dependent process. If such a reaction were a dominant one in the mechanism I_4/I_1 can be evaluated from the best straight line through the data of Fig. 5, utilizing equations (III) and (V). The value thus obtained from the results at 25°C is 12. Electron-impact data have shown that the minimum potential for oxygen-atom formation lies between 6.3 and 9 ev (1, 14). From photochemical data, ozone is decomposed by radiation of about 1 ev. If a plasma electron temperature, T_e, of about 25,000°K is assumed, the ratio of the number of electrons capable of exciting O_3 to those capable of exciting O_2 is (assuming a Maxwellian distribution)

$$\exp(\Delta E/RT_e)$$

or about 20, which is of the order of the value found for I_4/I_1. The above argument is completely qualitative and is merely presented to show that the value of I_4/I_1 is not inconsistent with present knowledge and does not rule out reaction (*d*) in the mechanism. Any quantitative treatment must, of course, consider also the relative cross sections for the two processes as shown in equation (IV), as well as require a more precise knowledge of the distribution function.

Approximately the correct pressure dependence for the steady-state ozone concentration may be obtained by assuming that the additional destruction reaction involves collision of ozone with an active species of oxygen formed in the discharge. Such a reaction must compete with a nearly pressure independent destruction reaction of the active species. The kinetics for this mechanism lead to a relation of the form of equation (III) in which the coefficient of $[O_3]_{ss}$ is independent of discharge current.

If, in such a mechanism, the active oxygen species represents an electronically excited molecule, the most plausible state is probably $^1\Sigma_g^+$. This state is highly metastable, having a lifetime for radiation of about 7 sec (15). It would thus be expected to disappear at the walls, rather than by radiation. Its energy, 1.6 ev, is enough to cause dissociation of $O_3[D(O_2 - O) = 1.0$ ev]. Since the transition involves a change in multiplicity, O_2' would not be formed directly in photolysis, but could be formed on electron impact by the well-known resonance-exchange process. Evidence for its occurrence has been obtained in controlled-speed electron bombardment of oxygen (16). O_2' may alternatively be representations of the type O_2^+ or O_2^-. For example, the reaction

$$O_2^+ + O_3 \rightarrow O_2 + O_3^+ \qquad (g)$$

followed by decomposition of O_3^+ on neutralization, might occur.

The possibility that ozone is destroyed in an energy chain similar to that postulated by Schumacher (17) and Heidt (18) seems remote in view of the low concentrations of ozone existing in the present experiments.

In conclusion, while the author's results cannot rule out conclusively the possibility that an ozone destruction step occurs in addition to that involving oxygen atoms, the data can be satisfactorily explained without such a step if the ozone formation step is considered in a detailed manner. From the point of view of simplicity, therefore, such a mechanism seems most plausible.

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Technical Reviews

The Oxygen Concentration Cell as a Factor in the Localized Corrosion of Metals

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ABSTRACT

Literature on the oxygen concentration cell has been reviewed. The discovery and early history of the cell are outlined, and environmental conditions favorable to its development are classified and discussed. Theories of the mechanism of the cell are presented. The current produced by an oxygen concentration cell is considered in terms of the open-circuit potentials and polarizing characteristics of the anode and cathode, and the resistance of the metal and electrolyte. Selected quantitative data are shown in tabular and graphic form.

In the same year that Volta announced his discovery of the battery, Haldane (1) found that its action ceased in vacuum or in nitrogen, and increased in oxygen, and Davy (2) showed that, when it was exposed to the atmosphere, oxygen was absorbed.

For a long time oxygen was supposed to act on the anodes, where it produced oxidation. However, when Grove (3) demonstrated that oxygen was consumed at the cathodes of his gas battery, it became apparent that oxygen could play a part different from the one hitherto assigned to it.

DISCOVERY AND EARLY HISTORY

Around 1845, Adie (4, 5) demonstrated the cathodic function of oxygen in a more convincing manner in the following experiments: "A piece of zinc was cut into two halves, and connected in the usual manner with a long wire galvanometer, the helix containing 2000 convolutions. The two plates of zinc were immersed in water, and arranged to allow a tube containing oxygen to be placed at pleasure over the upper portion of either plate. After completing the connections, a short time was allowed for the galvanometer to reach zero; the tube filled with oxygen was then inverted over one of the plates which immediately deflected the galvanometer showing the *oxygenated plate to be the negative element of the couple*. The tube was now passed over from the negative zinc to the positive piece, when, in the course of a few minutes, the galvanometer again shewed the new oxygenated zinc to be acting the part of a negative or platinode plate. The deflections of the needles were from 15° to 20°, where they remained steadily for some time. Instead of placing a tube of oxygen over one of the plates, if the water in front of one be stirred carefully with a quill, or if the plate be attached to an elastic wire, and made to vibrate in the water, it is immediately oxygenated more rapidly than the opposite one, and becomes strongly negative. The vibrated plate forms a very beautiful experiment. Like results were obtained with two pieces of iron.

.....

"Two slips of zinc cut side by side from the same sheet were placed in a running brook, the one opposed to a rapid part of the current, the other in a still place at the edge. Connecting these in the usual manner with the galvanometer, there was a permanent deflection of 25°; and on changing the respective places of the plates in the stream without disturbing their attachments to the galvanometer, the needles immediately passed to the opposite side of the card; in both cases the piece of zinc in the current acted as a negative or platinode plate. . . . It is the greater supply of oxygen to the plate in the current which converts it into a negative or platinode. A cell containing two small silver wires and the cyanide of silver solution used for electro-plating was attached in place of the galvanometer, when, after a lapse of two hours, metallic silver was seen precipitated in a minute quantity on the silver wire connected with the piece of zinc in still water.

"Two plates of iron were placed in the stream under like conditions to the zinc; after two hours metallic silver was distinctly seen precipitated on the silver wire connected with the iron plate in still water.

.....

"A single plate of iron exposed to water and oxygen gas has local differences on its surface which act in the same way as if the iron had been in two halves and placed in a stream in the manner described. . . ."

Prior to Adie's experiments, Zamboni (6) had found that a partially immersed strip of tin, zinc, or copper was cathodic to a strip of the same metal fully immersed, and Marianini (7) had made experiments in which he obtained momentary differential aeration currents by lifting one of two electrodes of zinc or copper into the air and replacing it in the electrolyte.

Additional evidence of the cathodic influence of oxygen was obtained by Viard (8) in 1852 by means of admirably planned and executed differential aeration experiments on a number of metals in water and aqueous solutions. In all experiments analogous results were obtained without exception.

In view of the observations of Adie and Viard, there is no reason why the effect of differential oxygen concentration in producing corrosion currents should not have been taken into account by subsequent investigators of corrosion. But the significance of the experiments was not grasped at the time, and later they were forgotten. In the latter part of the nineteenth century and the early part of the present one, the opinion was expressed by those who advocated the electrochemical theory of corrosion that heterogeneity of the metal, or other factors relating to the metal, such as differential stress, were the sole causes of corrosion currents.

Conditions Favorable to Development

In 1915, Aston (9) took exception to this viewpoint, and called attention to the importance of heterogeneity of the contacting liquid. To illustrate, he cited an experiment in which an appreciable electromotive force was produced between two electrically connected bars of steel in a beaker of water through which air was bubbled, when one of the bars was wrapped with a few thicknesses of cloth. He explained the result on the basis of the differential aeration principle, and remarked that porous iron rust acts similarly to the cloth in screening oxygen, with the result that areas of iron underlying patches of porous iron rust are anodic to adjacent areas of unrusted iron, resulting in conditions favorable to pitting. As shown by Chappell (10), if iron under water is completely covered with rust, corrosion will be retarded, since the rate of diffusion of oxygen to the surface of the metal will be everywhere reduced.

Around 1923–1925, Evans (11–18) made a comprehensive and detailed study of the oxygen concentration cell,[1] and repeatedly stressed its importance as a potential cause of intense localized corrosion. In this country, the common occurrence of the cell and its destructive nature were emphasized by McKay (19).

As shown experimentally by Evans (11), the effect of restricting access of oxygen to a part of the surface of the metal is not to increase the total corrosion, but to concentrate on the nonaerated area the corrosion which would otherwise be distributed over the surface. Evans (11) also demonstrated that, at such places that are anodic owing to the absence of oxygen, the product of corrosion is generally a soluble salt. Secondary corrosion products are usually precipitated at a sensible distance from either the anode or cathode, and do not protect the metal from further attack. For these reasons, the rate of corrosion produced by an oxygen concentration cell may be dangerously high.

Conditions favorable to the development of oxygen concentration cells commonly exist in crevices, under porous deposits of corrosion products or foreign substances, in soils, at water lines, under drops of water or aqueous solutions, and in regions of unequal liquid velocities.

As early as 1840, Mallet (20) observed that clean iron immersed in water oxidized preferentially at the point of contact of a glass lens of large curvature, or at a very acute angle formed between a plate of iron and a plate of glass, or between two plates of iron. Subsequently, others made analogous observations. A rational explanation of corrosion in crevices was first given by Evans (11) on the basis of electrochemical principles. Ellis and LaQue (21), in tests on Type 430 stainless steel in flowing sea water, secured data showing that attack within a crevice increases in proportion to the increase of area of the freely exposed metal outside.

From 1819 (22) onward, the opinion was repeatedly expressed that rust accelerates subsequent rusting by virtue of the fact that iron oxide is cathodic to iron. It is not in doubt that rust can act in this manner (23, 24) but, as first demonstrated by Aston (25), a localized deposit of porous rust plays a different role. By hindering diffusion of oxygen, it renders the surface of the underlying iron anodic to the surrounding surface to which oxygen has better access.

Aside from acting as a mechanical oxygen-screen, rust can also produce chemical oxygen-screening by combining with oxygen dissolved in the liquid. By means of direct measurement of oxygen advance, Evans and Mears (26) showed that corrosion products of several kinds delayed the passage of oxygen considerably. Diffusion of oxygen through ferrous hydroxide was extremely slow, undoubtedly because the precipitate absorbed oxygen in its conversion to hydrated magnetite and ferric oxide. Other corrosion products capable of oxidation are in the same category. For example, May (27), in discussing the mechanism of the pitting of copper in water containing chlorides, said: "There is little doubt that the outward diffusion of cuprous chloride in solution from the anode is a most important factor in maintaining rapid pitting, since by reacting with the oxygen diffusing into the pit it can maintain the oxygen concentration at the anode at the lowest possible value." May also observed that the higher rates of pitting are associated with the formation of solid cuprous chloride in a highly porous state. Conversely, deposition of cuprous chloride in a compact layer with a high electrical resistance favors stifling.

Differential aeration currents are an important factor in the corrosion of metal underground. Variations in the oxygen content of soil in contact with a pipe or other metallic structure may be produced by local differences in its texture, degree of compactness, or moisture content. Denison (28) designed a laboratory soil corrosion cell in which a potential difference was developed by differential aeration between two electrodes of the same material separated by moist soil as the electrolyte. Cells constructed on this principle have been used to measure the rate of corrosion of metals and alloys for correlation with the rate of corrosion of specimens in field tests, and with the rate of corrosion of a pipe-line system (29–32). A modification of the cell has been described by Schwerdtfeger (33).

Distribution of attack on metal partly immersed in stagnant water or salt solution and partly exposed to air or oxygen is usually determined to a large extent by differential aeration. At or near the water line, where the oxygen required for the cathodic reaction is readily replenished, a cathodic zone commonly develops that is immune. The lower part of the metal, to which oxygen has less access, becomes anodic and is corroded In 1932,

[1] Known also as the differential aeration cell and the Evans cell.

Evans and Hoar (34) showed that the velocity of corrosion is quantitatively equivalent to the strength of the electric currents which flow between the cathodic region at the water line and the anodic region below it. This outstanding pioneer work gave quantitative confirmation of the electrochemical theory of corrosion.

In experiments by Evans and co-workers (34–36), it was found that practically the entire cathodic reaction was confined to the neighborhood of the meniscus. The area shown to be anodic by electrical measurements coincided with the area visibly attacked.

Conditions analogous to those existing at a water line are produced by drops of aqueous liquid on a metal surface. Corrosion develops, in most cases, below the center of the drop; below the marginal portion the metal remains unattacked.

The passage of differential aeration currents between the marginal and central parts of a drop was demonstrated by Baisch and Werner (37). It was shown by Evans (38) that, if the periphery of a drop is surrounded by nitrogen, and oxygen is blown down the center, an uncorroded center surrounded by a corroded ring develops instead of the reverse normal distribution.

The strength of an oxygen concentration cell is increased by motion of the liquid. Motion increases rate of diffusion of oxygen to the cathodic surface. Cathodic polarization is decreased, and corrosion rate is increased.

Increased rate of oxygen diffusion also increases the open-circuit potential of the cathode. Wormwell, Nurse, and Ison (39), Mansa and Szybalski (40), and Cohen (41) have found that the potential of iron in fresh water becomes increasingly more cathodic with increase in velocity up to a limiting velocity, after which further increase in velocity does not change the potential. By means of differential velocity, Cohen obtained a potential difference as high as 0.70 v.

Motion of the liquid not only increases rate of transfer of dissolved oxygen from the bulk of the solution to the surface of the cathode, but also increases rate of transfer of metal ions from the surface of the cathode to the bulk of the solution. When the anode is shielded from the motion, the effect of the latter opposes that of the former, due to increase in strength of both the oxygen concentration cell and the opposing metal ion concentration cell. Usually, the oxygen concentration cell dominates, but in the case of a noble metal, such as copper, the effect of removal of metal ions may preponderate (11, 42–44). The principal determining factors are the difference in oxygen concentration and the velocity. As the difference in oxygen concentration increases, the velocity of the liquid required to cause reversal from an oxygen concentration cell to a metal ion concentration cell also increases.

When velocity and turbulence of the liquid are sufficiently high to remove or prevent formation of a film of insoluble corrosion product on the cathode, the type of attack changes to erosion-corrosion. This is reflected by a drop in potential (44).

Cell Mechanism

In 1849, Adie (45) expressed the opinion that the electromotive force of the oxygen concentration cell is created by metal oxide produced at the aerated surface, acting as cathode, and metal at the unaerated surface, acting as anode. To test this viewpoint, a piece of zinc was cut into halves. One of the halves was oxidized by heat, and then formed into a couple with the bright half. On immersion in water, a galvanometer indicated that the oxidized half was the cathode. Similar results were obtained with iron, copper, and lead.

Much later, Adie's theory was strengthened by the observation of Lorenz and Hauser (46) that lead, silver, nickel, copper, iron, and zinc, when used as electrodes surrounded with oxygen at a pressure of one atmosphere, and in sodium hydroxide or sodium sulfate solution, show potentials almost identical with those of their oxides in the same solution.

Evans (11, 15) considered that two different mechanisms are possible, the first one that the oxygen concentration cell functions as a metal-metal oxide cell, and the second one that the cathodes of the cell consist of comparatively noble spots on the aerated area, created by impurities or lack of physical uniformity. If the second mechanism is operative "the alkali formed over the cathodic particles will spread over the iron around them, and here the principal anodic product will be a thin and invisible film of iron hydroxide; in other words, the iron in this outer portion will become passive and cease to pass into solution." Thus the second mechanism would lead to the first one. "If foreign particles were completely absent, this state of affairs would never be set up, and we should expect to get no corrosion unless the first mechanism comes into play." On the basis of special experiments, Evans concluded that both mechanisms can play a part in producing a current. Evans (18) also remarked that "since in an ordinary differential aeration cell a current is produced immediately air is bubbled into one compartment, it is clear that no oxide film of any sensible thickness is needed for the partial ennoblement of the aerated electrode. It is likely that a layer of adsorbed oxygen (such as would be formed almost instantaneously) is sufficient to cause a slight alteration in potential."

Later, Evans (47–50) said that differential aeration currents can be referred to differences in the state of repair of an oxide film on the metal surface. The potential is slightly higher at the aerated places, where the film is kept in good repair by the conjoint action of dissolved oxygen and cathodically produced hydroxyl ion.

When a metal is covered with an oxide film, it may have any potential between that of the bare metal and the solid oxide (51). If the film is highly discontinuous, the potential will be almost as low as that of the film-free metal. As the film becomes more continuous, the potential rises toward that of the solid oxide. Presumably, if the film were perfect in its ability to prevent metal ions from entering the liquid, its potential would be that of a reversible oxygen electrode (47, 51, 52).

The lower potential of an imperfect oxide film is due to polarization caused by local currents flowing between anodes located at pores, lattice defects, cracks, or other weak spots in the film, and adjacent cathodes located on sound film. In an oxygen concentration cell, the film on the area accessible to dissolved oxygen is kept in better

repair than on the area shielded from oxygen, making the former cathodic to the latter.

The ennoblement by dissolved oxygen of the potentials of chromium, stainless steels, iron, titanium, and some other metals and alloys has been attributed by Uhlig (53–55) to a chemisorbed film of oxygen.

Thermodynamic origin of the electromotive force of the oxygen concentration cell has been stressed by McKay (19, 56, 57). From this viewpoint, the source of the electrical energy of the cell is found in the tendency of the differential concentration of oxygen to equalize, the energy relationship being such that the area of metal under the higher concentration of oxygen must be cathodic. An oxide film, if present, is influential in determining the amount of current produced.

Current Determining Factors

The current produced by an oxygen concentration cell is determined by the open-circuit potentials, and polarizing characteristics of the anode and cathode, and the resistance of the electrolyte and metal. It is equal to the difference between the polarized potentials of the cathode and anode divided by the sum of the resistances of the electrolyte and metal. In most cases, the resistance of the metal is negligibly small.

It is generally not possible to determine the open-circuit and polarized potentials and current flow on a naturally corroding metal surface, since the local anodes and cathodes cannot be identified and isolated. In the case of differential aeration, this was first accomplished by Evans and Hoar (34) for iron partly immersed in dilute potassium chloride solution. The current measured accounted for the whole of the corrosion of the anodic area as measured by the estimation of iron in the corrosion product. Later, differential aeration currents on zinc in sodium chloride or sodium sulfate solution were measured by Agar (58) by an independent method.

Open-Circuit Potentials

The open-circuit electromotive force of oxygen concentration cells may be evaluated indirectly by means of electrode potential measurements made in oxygen-free and in air- or oxygen-saturated solutions, or in solutions of different oxygen content. A number of such measurements are contained in the literature. A selected list is given in Table I.

The influence of hydrogen ion concentration on the electrode potential of iron has been investigated by Reiller (65), using deaerated and aerated solutions of hydrochloric acid, 0.5*N* NaCl, and NaOH. The data (Fig. 1) show that the electromotive force of an oxygen concentration cell increases with increase in *p*H of the solution. However, above a *p*H of about 9.5, the electromotive force is unstable, since a trace of oxygen at the anode is sufficient to make its open-circuit potential much more cathodic (65).

With reference to the dependence of potential on *p*H, it should be noted that the *p*H of the solution is altered by the cell current. For example, Reiller (65), using a laboratory type of oxygen concentration cell with iron electrodes in 0.5*N* NaCl solution, found that, in course of time, the *p*H at the anode decreased to 4.5 due to formation there of ferrous chloride, whereas the *p*H at the cathode increased to 11 due to the presence of cathodically produced NaOH.

At any *p*H value, the potential of an aerated electrode may be affected to a marked degree by the nature of the

TABLE I. *Effect of dissolved oxygen on electrode potential*

Metal	Solution	Potential (normal hydrogen scale) in volts			Difference (v)	Reference
		Deaerated	Air-saturated	Oxygen-saturated		
Aluminum	1*N* H_2SO_4	−0.41	−0.19		0.21	(59)
Aluminum	1*N* KCl	−0.88		−0.53	0.35	(60)
Copper	1*N* HCl	−0.03		0.04	0.07	(61)
Copper	0.2*N* H_2SO_4	0.20		0.28	0.08	(62)
Copper	1*N* KCl	−0.03		0.05	0.08	(63)
Copper	1*N* KOH	−0.30		−0.05	0.25	(61)
70-30 Brass	Sea water	−0.04	0.01		0.05	(64)
70-30 Cupronickel	Sea water	−0.01	0.04		0.05	(64)
Iron	0.1*N* HCl	−0.18	−0.16		0.02	(65)
Iron	0.05*N* H_2SO_4	−0.28	−0.25		0.03	(66)
Iron	0.5*N* NaCl	−0.44	−0.08		0.36	(65)
Iron	0.1*N* Na_3PO_4	−0.66	0.11		0.78	(67)
Iron	0.1*N* Na_2CO_3	−0.60	0.17		0.77	(66)
Iron	0.1*N* Na_2SiO_3	−0.68	0.03		0.71	(67)
Iron	0.1*N* NaOH	−0.70	0.08		0.78	(67)
Iron	1*N* NaOH	−0.72	0.00		0.72	(68)
18-8 Stainless steel	0.25*N* H_2SO_4	−0.07	0.56		0.63	(69)
18-8 Stainless steel	0.25*N* H_2SO_4	−0.07		0.60	0.67	(69)
18-8 Stainless steel	4% NaCl	−0.11	0.35		0.46	(70)
18-8 Stainless steel	4% NaCl + 0.3*N* NaOH	−0.02	0.05		0.07	(55)
Titanium	1*N* HCl	−0.30	0.08		0.38	(71)
Titanium	5*N* HCl	−0.38	−0.30		0.08	(71)
Titanium	1*N* H_2SO_4	−0.43	0.28		0.71	(59)
Titanium	3% NaCl	0.11	0.44		0.33	(71)

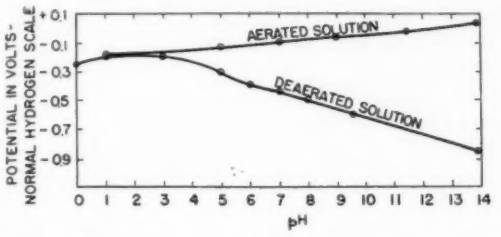

FIG. 1. Effect of *p*H on the electrode potential of iron in solutions of HCl, 0.5*N* NaCl, and NaOH. After Reiller (65).

TABLE II. *Effect of anions on electrode potential at constant p*H *in aerated solutions*

Metal	Solution	*p*H	Potential (normal hydrogen scale) in volts	Reference
Aluminum	1*N* NaCl + HCl	3	−0.50	(72)
Aluminum	1*N* Na_2SO_4 + H_2SO_4	3	−0.21	(72)
Aluminum	1*N* NaCl	7	−0.47	(72)
Aluminum	1*N* Na_2SO_4	7	−0.11	(72)
Copper	HCl	0	0.05	(73)
Copper	H_2SO_4	0	0.22	(73)
Copper	HCl	3	0.25	(73)
Copper	H_2SO_4	3	0.24	(73)
Copper	1*N* NaCl	7	−0.01	(73)
Copper	1*N* Na_2SO_4	7	0.23	(73)
Copper	0.01*N* NaCl	7	0.19	(73)
Copper	0.01*N* Na_2SO_4	7	0.25	(73)
Iron	0.1*N* NaCl	7	−0.30	(74)
Iron	0.1*N* CH_3COONa + CH_3COOH	7	0.14	(74)
Iron	0.1*N* Na_2HPO_4 + H_3PO_4	7	0.03	(74)
Iron	Na_2CO_3	9.5	0.13	(66)
Iron	Na_2CO_3 + 1% Na_2SO_4	9.5	−0.30	(66)
Iron	Na_2CO_3 + 1% NaCl	9.5	−0.30	(66)
Iron	Na_2CO_3	11	0.17	(66)
Iron	Na_2CO_3 + 1% Na_2SO_4	11	0.14	(66)
Iron	Na_2CO_3 + 1% NaCl	11	−0.30	(66)
Iron	NaOH	11	−0.12	(66)
Iron	NaOH	12	−0.02	(66)
Iron	NaOH + 1% Na_2SO_4	12	−0.38	(66)
Iron	NaOH	13	−0.02	(66)
Iron	NaOH + 1% Na_2SO_4	13	−0.03	(66)
Iron	NaOH + 1% NaCl	13	−0.04	(66)

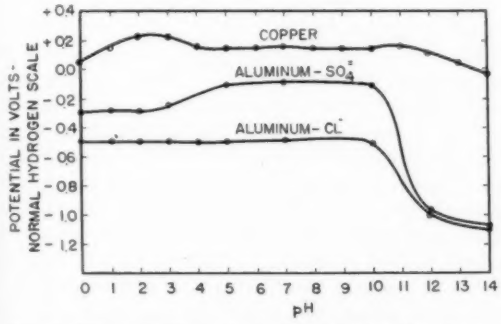

FIG. 2. Effect of *p*H on electrode potential. Aluminum in aerated 1*N* NaCl + HCl or NaOH, and 1*N* Na_2SO_4 + H_2SO_4 or NaOH. Copper in aerated 0.01*N* NaCl + HCl or NaOH. After Akimov, Glukhova, and Rosenfel'd (72, 75).

anion or anions in the electrolyte. This is illustrated in Table II.

The relationship between hydrogen ion concentration and electrode potential for aluminum in aerated 1*N* NaCl plus HCl or NaOH, and 1*N* Na_2SO_4 plus H_2SO_4 or NaOH has been determined by Akimov and Glukhova (72), and the same relationship for copper in aerated 0.01*N* NaCl plus HCl or NaOH has been determined by Akimov and Rozenfel'd (75). Data are given in Fig. 2.

Anodic Polarization

Anodic polarization is produced by development of insoluble, protective corrosion products on the surface of the anode, or by accumulation of ions released from the anode in the adjacent liquid.

Since dissolved oxygen is required for formation of most protective films, film polarization usually does not occur when dissolved oxygen is absent at the anode, or present in very small amount.

As previously mentioned, the potential of copper is appreciably increased by small increase in copper ion concentration. On the other hand, less noble metals such as iron and aluminum are relatively unaffected by changes in ionic concentration, and consequently are not subject to concentration polarization.

Cathodic Polarization

The current flowing in an oxygen concentration cell is usually controlled by polarization of the cathode. The shape of the cathodic polarization curve may be influenced by: composition, surface condition and dimensions of the cathode, composition, temperature, and movement of the solution, and difference between concentration of oxygen in the bulk of the solution and that at the cathode surface.

If oxygen is consumed at the cathode as fast as it arrives by diffusion, the rate of its arrival is the controlling factor. If oxygen reaches the cathode at a rate faster than its rate of consumption, the rate of its cathodic reduction is in control. In the second case polarization is strongly dependent upon the composition and surface state of the cathode, and the polarization curve is determined by the oxygen reduction overvoltage, which may be expressed by Tafel's equation for hydrogen overvoltage (52, 76).

The presence of film or scale on the surface of the cathode may have an important influence on the shape of the cathodic polarization curve. If the deposit possesses no electronic conductivity, and cannot itself function as cathode, it acts to hinder diffusion of oxygen to the metal surface. If it exhibits good electronic conductivity, then the course of the polarization curve in the region of oxygen ionization depends on the value of overvoltage of the deposit itself. If it exhibits poor electronic conductivity compared with the metal, then the measured potential is affected by the value of the potential drop due to the ohmic resistance of the deposit. As a result, there will be some shift in the curve for cathodic polarization toward more anodic values. The magnitude of this *IR* drop has been determined for several cathodically polarized systems by Brown, English, and Williams (77).

TABLE III. *Current density required to decrease open-circuit potential of cathode by* 0.1, 0.3, *and* 0.5 *v*

Metal	Solution	Cathodic current density (amp × 10^{-5}/cm²)									Reference
		Stagnant solution			Moving solution						
		Difference between open-circuit and polarized potential of cathode (v)									
		Air atmosphere			Air atmosphere			Oxygen atmosphere			
		0.1	0.3	0.5	0.1	0.3	0.5	0.1	0.3	0.5	
Aluminum	Buffered[a] 0.02*N* NaCl, *p*H 5	1	2	3[c]							(85)
Aluminum	0.02*N* NaCl	0.3	0.5	0.7							(85)
Aluminum	0.5*N* NaCl					4[d]	8[d]	10[d]	23[d]	32[d]	(86)
Aluminum	Buffered[b] 0.5*N* NaCl, *p*H 9							18[d]	94[d]	160[c, d]	(86)
Duralumin	0.5*N* NaCl	4	10	48[c]	24[d]	30[d]	44[c, d]				(86)
Copper	0.05*N* K_2SO_4 + 0.002*N* H_2SO_4	0.8	1	1							(87)
Copper	0.05*N* K_2SO_4 + 0.01*N* H_2SO_4	0.6	1	1							(87)
Copper	0.05*N* K_2SO_4	0.4	2	2							(87)
Copper	0.1*N* KCl	0.5	2	3							(87)
Copper	3% NaCl				10[e]	16[e]	19[e]				(83)
Copper	Sea water				10[f]	42[f]					(88)
Copper	Buffered[b] 0.5*N* NaCl, *p*H 9					10[d]	28[d]	5[d]	40[d]	150[d]	(89)
Aluminum brass	Sea water				8[f]	22[f]					(90)
90-10 Cupronickel	Sea water				7[f]	18[f]					(91)
70-30 Cupronickel	3% NaCl				1[e]	3[e]	6[e]				(83)
Iron	0.05*N* K_2SO_4 + 0.01*N* H_2SO_4	6	40	56[c]							(92)
Iron	0.05*N* K_2SO_4 + 0.001*N* H_2SO_4	2	4	20[c]							(92)
Iron	0.5*N* NaCl + 0.01*N* HCl							149[d]	250[c, d]		(93)
Iron	0.05*N* K_2SO_4	1	4	15[c]							(92)
Iron	0.1*N* KCl				13[g]	15[g]	25[c, g]				(49)
Mild steel	Sea water	0.9	7[c]		16[f]	17[f]	21[c, f]				(94)
Iron	Buffered[b] 0.5*N* NaCl, *p*H 9				18[d]	32[d]	44[d]	44[d]	150[d]	182[d]	(90)
Iron	0.05*N* K_2SO_4 + 0.01*N* NaOH	1	3	4							(92)
Iron	0.5*N* NaCl + 0.01*N* NaOH							2[d]	20[d]	120[d]	(93)
Iron	0.1*N* NaOH	0.1	0.3	2							(92)
18-8 Stainless steel	Sea water					0.5[f]	42[f]				(89)
18-8 Stainless steel	Buffered[b] 0.5*N* NaCl, *p*H 9								0.8[d]	80[d]	(93)
Titanium	0.5*N* NaCl				0.003[h]	0.006[h]	0.3[h]				(95)
Titanium	Sea water					0.3[f]	3[f]				(89)

[a] 1% CH_3COONa + CH_3COOH.
[b] 25 × 10^{-3}*N* Na_2CO_3 + 5 × 10^{-3}*N* $NaHCO_3$.
[c] Hydrogen evolution region of polarization curve.
[d] Solution stirred at 2000 rpm.
[e] Solution flowing at 0.8 ft/sec.
[f] Sea water flowing at 7.8 ft/sec.
[g] Solution stirred at 15 rpm.
[h] Electrode moving at 0.1 ft/sec.

Polarizing characteristics of oxygen concentration cells may be evaluated by means of experimentally determined polarization curves. In solutions of low electrical resistivity, the corrosion current is approximately determined by the point of intersection of the anodic and cathodic curves. As the resistivity of the solution increases, the amount of current flowing lags more and more behind the intersection point, since an increasing residual electromotive force is needed to overcome the resistance of the solution. Only a limited number (49, 78–84) of polarization curves have been determined under conditions that are relevant to those existing in an oxygen concentration cell. No study has been made of the polarizing characteristics of a metal as a function of dissolved oxygen, *p*H, cation, velocity, and temperature. If reliable data of this type were obtained, it should be possible to predict satisfactorily the behavior of an oxygen concentration cell under a wide variety of conditions.

When the anode of an oxygen concentration cell does not polarize, and the resistance of the solution is not high, which is a common case, the limiting corrosion current is reached approximately when the difference between the open-circuit and polarized potential of the aerated cathode is equal to the open-circuit electromotive force of the cell. Therefore, in this case, when the open-circuit potentials and cathodic polarization curve are known, the cell current may be determined. In Table III, values of applied cathodic current density are given for differences between the open-circuit and polarized potentials of the cathode of 0.1, 0.3, and 0.5 v.

The effect of velocity on the cathodic polarization of mild steel in sea water (90) is shown in Table IV.

TABLE IV. *Effect of velocity on the cathodic polarization of mild steel in sea water at 26°C. Reference (90)*

Velocity of sea water	Current density (amp × 10^{-5}/cm²). Difference between open-circuit and polarized potential (v)	
	0.1	0.3
ft/sec		
0.0	2	4
0.5	4	5
3.0	7	9
5.0	10	12
7.8	13	14
9.0	19	21
13.0	31	32

Cell Current Measurements

Using an oxygen concentration cell with iron electrodes in 0.5*N* NaCl solution, Reiller (65) determined the influence of temperature on current output and open-circuit potentials. The relationships are shown in Fig. 3. By means of further experiments, Reiller showed that increase in cell current with increase in temperature was due partly to decrease in resistance of the electrolyte, and partly to decrease in cathodic polarization.

The variation in the current output of an oxygen concentration cell with iron electrodes in 0.5*N* NaCl solution as a function of the relative areas of the anode and cathode was determined by Herzog (96). Results are shown in Fig. 4.

Herzog and Chaudron (97) found that the current produced by an oxygen concentration cell with iron electrodes in sea water was only 38% of that produced in 3% NaCl solution. They considered that the lower current in sea water was due to the partially protective action of cathodically deposited magnesium and calcium carbonates.

The influence of surface preparation of the cathode on cell current was shown by Wickert and Wiehr (98) for iron in 0.1*N* NaCl solution. A relatively smooth cathode surface obtained by polishing gave a significantly higher cell current than did a filed surface. When a polished iron cathode and a constant $Cd/CdSO_4$ anode were used, with oxygen aeration in the cathode vessel, variation of the *p*H of the NaCl solution gave results as follows: beyond the range of hydrogen evolution, the cell current was a

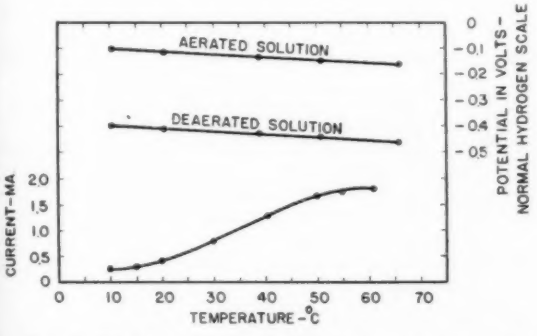

Fig. 3. Effect of temperature on the current output and open-circuit potentials of an oxygen concentration cell with iron electrodes in 0.5*N* NaCl solution. After Reiller (65).

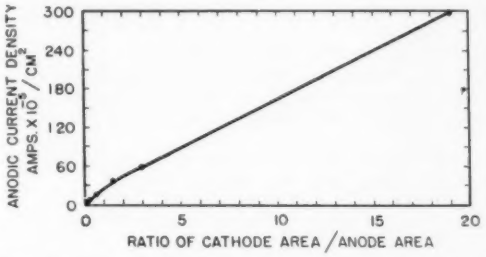

Fig. 4. Effect of relative area of the electrodes on the current produced by an oxygen concentration cell with iron electrodes in 0.5*N* NaCl solution. After Herzog (96).

maximum in the neighborhood of *p*H 7; above *p*H 8, current gradually decreased with increase in *p*H value.

Discussion

Data on the electrochemical behavior of oxygen concentration cells are scattered and limited in scope. Therefore, it is not possible to generalize to any extent on the basis of interpretation and correlation of published results. However, from the data in Tables I–IV, and Fig. 1 and 2, and from other data not included therein, certain generalizations, which may be subject to exceptions, appear to be justified. Among these are the following.

In the case of iron, open-circuit emf and cathodic polarization increase with increase in *p*H value. Activity of the cell is greatest in a *p*H range of about 5 to 9. In acid solutions, cell current is limited by lack of sufficient electromotive force, and, in alkaline solutions, by strong cathodic polarization. Movement of the liquid at the cathode results in increase in open-circuit potential and decrease in polarization.

In acid and neutral solutions, the emf of aluminum and 18-8 stainless steel is high in relation to that of copper.

In acid solutions, copper polarizes more readily than iron or aluminum. In neutral solutions, copper polarizes more readily than iron, but less readily than aluminum. Titanium polarizes with outstanding rapidity. Cathodic polarization of aluminum, copper, and 18-8 stainless steel is decreased by movement of the liquid.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1957 Journal.

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FUTURE MEETINGS OF
The Electrochemical Society

Cleveland, September 30, October 1, 2, 3, and 4, 1956

Headquarters at the Statler Hotel

Sessions will be scheduled on

Batteries, Corrosion, Electrodeposition,
Electronics—Semiconductors,
Electrothermics and Metallurgy, Theoretical
Electrochemistry (joint with Electrodeposition),
and Theoretical Electrochemistry

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Washington, D. C., May 12, 13, 14, 15, and 16, 1957

Headquarters at the Statler Hotel

★ ★ ★

Buffalo, October 6, 7, 8, 9, and 10, 1957

Headquarters at the Statler Hotel

★ ★ ★

New York, April 27, 28, 29, 30, and May 1, 1958

Headquarters at the Statler Hotel

★ ★ ★

Ottawa, September 28, 29, 30, October 1, and 2, 1958

Headquarters at the Chateau Laurier

★ ★ ★

Current Affairs

Candidates for Society Offices–1957-1958

NORMAN HACKERMAN

I. E. CAMPBELL

R. A. SCHAEFER

A. L. SMITH

The Nominating Committee, W. Duckworth, H. M. Scholberg, A. E. Middleton, M. J. Udy, and R. M. Burns, Chairman, appointed by President Hans Thurnauer, having met at San Francisco, Calif., during the 109th Meeting of The Electrochemical Society, presents the following list of candidates for office for the term 1957–1958:

For President—

Norman Hackerman

For Third Vice-President—

I. E. Campbell

R. A. Schaefer

A. L. Smith

These candidates have been notified, and each has expressed his willingness to run for office and to serve if elected.

The two other Vice-Presidents, Sherlock Swann, Jr., and W. C. Gardiner, since they were elected for a three-year term, will automatically become first and second Vice-President, respectively.

The above slate will be voted on in the fall ballot-by-mail election—the successful candidates to assume office in the spring of 1957.

Norman Hackerman

Presidential Candidate

Norman Hackerman, Professor of Chemistry, Chairman of the Department, and Director of the Corrosion Research Lab. at the University of Texas, Austin, Texas, was born in Baltimore, Md., in 1912. He received all of his college training, including graduate work, at Johns Hopkins University, receiving the PH.D. degree in physical chemistry in 1935. Thereafter he was appointed assistant professor of chemistry at Loyola College in Baltimore, later serving as research chemist for the Colloid Corp. in that city. In 1941 he was appointed assistant professor of chemistry at Virginia Polytechnic Institute, which he left in 1944 to work on the Manhattan Project.

Dr. Hackerman joined the staff of the University of Texas in 1945. His research interests deal principally with the chemistry and physics of surfaces, especially as these phenomena apply to metal corrosion. He and his students have published numerous articles on adsorption on metal surfaces and its influence on electrochemical properties and reactivity, and on the passivity of metals.

A member of The Electrochemical Society since 1943, Dr. Hackerman served as Chairman of the Corrosion Division in 1951, and has been Technical Editor of the JOURNAL since 1950. He belongs to the American Association for the Advancement of Science, and was the 1950 Chairman of the Gordon Corrosion Research Conference. He also holds memberships in Phi Lambda Upsilon, Sigma Xi, The Faraday Society, the American Chemical Society, and the National Association of Corrosion Engineers, serving on the Board of Directors for the latter. He is a member of the Board of Editors of the Chemical Monograph Series of the American Chemical Society, and is Chairman of the Intersociety Corrosion Committee, 1956–58.

I. E. Campbell

Vice-Presidential Candidate

Ivor E. Campbell is Chief of the Division of Inorganic Chemistry and Chemical Engineering of the Battelle Memorial Institute in Columbus, Ohio. He was born in Kenton, Ohio, in 1919, and received his undergraduate training in chemistry and mathematics at Evansville College in Evansville, Ind., and his graduate training at The Ohio State University, from which he received the Ph.D. degree in inorganic chemistry in 1943.

Dr. Campbell joined the Battelle staff as a research chemist in 1943. He was made assistant supervisor of the Division of Nonferrous Metallurgy in 1948 and was named to his present position in 1950.

He is the author of over 30 papers in various scientific and trade journals. These papers deal principally with vapor plating and with the properties of high-purity metals. He is coauthor of The Electrochemical Society's monograph "Vapor Plating" published in 1955, and Editor of "High Temperature Technology" published by John Wiley, as a part of the Society's monograph series, in 1956.

Dr. Campbell's major present interests, as indicated by his publications, have been in the development of improved processes for the preparation of high-purity metals and in the formation of refractory coatings by vapor-deposition techniques. He has worked extensively with iodide-refining processes for metals, and has presented at

Society meetings a number of papers on the preparation of high-purity metals by the iodide process.

Dr. Campbell joined The Electrochemical Society in 1944. He served as Secretary-Treasurer of the Electrothermics Division from 1949–53, Chairman of the Division from 1953–55, and at present is a member of the Executive Committee of the Division. He was Chairman of the Bylaws Committee of the Society in 1954 and 1955, and at present is Chairman of the Becket Memorial Award Committee.

During Dr. Campbell's term as Chairman, the Electrothermics Division merged with the Rare Metals Group of the Electronics Division to form the Electrothermics and Metallurgy Division. The establishment of the Becket Memorial Award for undergraduate students demonstrating proficiency in the field of electrothermics was initiated by the Electrothermics and Metallurgy Division during his term as Chairman.

R. A. Schaefer

Vice-Presidential Candidate

Ralph A. Schaefer, Technical Advisor to the President of the Cleveland Graphite Bronze Div. of the Clevite Corp., Cleveland, Ohio, was born in Grafton, Ohio, in 1913. He studied chemical engineering at the University of Notre Dame, transferring to Western Reserve University in Cleveland where he received an A.B. degree in 1935 and an M.S. degree in 1936.

In the spring of 1936 he joined the laboratory staff of the Cleveland Graphite Bronze Co. and has remained with this company ever since. He continued his studies at Western Reserve and received a Ph.D. degree in physical chemistry in 1941. He became the company's first Director of Research in 1945, Vice-President and Materials Development Director of a development division of the parent company in 1953, and late in 1955 was appointed to his present position.

His work with the company included metallurgical developments in the production of composite bimetal and trimetal bearings, metal cleaning, pickling, fluxing, and casting on continuous processes. He also worked in the field of powder metallurgy on clutch plates and friction elements which were used in large volume by the aircraft industry during the war. In 1940 his company embarked on an extensive research program to investigate electrodeposition as a fundamental process for bonding bearing materials to steel. Dr. Schaefer was chosen to captain the venture, and, because of this introduction to electrochemistry, he likes to consider himself a practical electroplater who entered the field by way of the back door. He was responsible for much of the early research and development work on heavy silver and babbitt type alloy overlay plated bearings. These plating processes have been particularly successful in engineering applications involving rotating or oscillating parts.

Dr. Schaefer is the author or coauthor of a substantial number of articles and the recipient of many patents, all dealing directly or indirectly with sleeve bearings. Of the many technical societies of which he is a member, he has been very active in the American Electroplaters' Society, having been a member of its Research Committee and Editorial Board, and Vice-President and President.

He has been active in the administrative affairs of The Electrochemical Society for the past ten years. In the Electrodeposition Division, he held several offices, including Chairman 1949–50. He served on the Editorial Board and was a contributor to the Second Edition of "Modern Electroplating." He has been active in the Cleveland Section's activities for many years and was Chairman of the Section during the 1950 Cleveland Convention. In recent years he has repeatedly been appointed to the Ways and Means Committee of the Society. At the Cincinnati Meeting he was appointed by President Uhlig to be Chairman of a Survey Committee whose function it was to study and make recommendations for improving the administrative operations of the Society. The report of this committee has in part already been adopted; other parts are under study for future incorporation. At present he is a member of the Ways and Means and Finance Committees of the Society.

A. L. Smith

Vice-Presidential Candidate

Arthur L. Smith, Manager of the Chemical and Physical Lab. of the Lancaster, Pa., plant of the Radio Corp. of America, was born in New York City in 1915. He received a B.S. degree in chemistry from Fordham University in 1941. From 1941 to 1943 he was a Teaching Fellow at Brooklyn Polytechnic Institute from which he obtained an M.S. degree in 1943. He then became a research associate at BPI, working in Dr. Roland Ward's group which held government contracts for the development of infrared sensitive phosphors for communication purposes. As a result of this research, and most particularly the development of the SrSe:Sm:Eu phosphor, he was awarded a Ph.D. in 1946.

Dr. Smith continued his work in the phosphor field upon joining RCA in 1945 as a member of the Phosphor Development Activity at Lancaster. Several years later he became Leader of this activity. A number of patents and papers on phosphors and their use in cathode-ray tubes resulted from this work; the papers were published almost entirely in the Society's JOURNAL and symposia. His main interest centered about the preparative conditions of phosphors as they influence their final properties, and in the search for new phosphor compositions. The chemistry of the activator center was also investigated. He has been Manager of the Chemical and Physical Lab. of RCA's Lancaster plant since 1954.

As a member of The Electrochemical Society for the past ten years, Dr. Smith has been an ardent supporter and booster of the symposia held each year by the Luminescence group. He was also directly involved in establishing the Oxide-Cathode and Semiconductor Symposia which have attracted worldwide attention and support. He has successively served as a member of the Committee on Luminescence, Vice-Chairman of the Luminescence section, and as Chairman of the Electronics Division.

Nine Members Appointed to National Science Board

Lawrence M. Gould, Paul M. Gross, George D. Humphrey, Edward J. McShane, Frederick A. Middlebush, Samuel M. Nabrit, Julius A. Stratton, Edward L. Tatum, and Warren Weaver have been appointed to the National Science Board. The United States Senate, on May 25, confirmed the appointments, following their nomination earlier by President Eisenhower. Doctors Gould, Gross, Humphrey, and Middlebush, Charter Members of the Board, were reappointed. Except for Dr. Weaver, all will serve terms of six years, ending May 10, 1962. The term of Dr. Weaver, who succeeds the late Reverend James B. Macelwane, S. J., expires May 10, 1960.

Acheson Medal Award to R. M. Burns

Robert M. Burns, formerly Chemical Director of Bell Telephone Labs., has been chosen to receive the Acheson Medal Award of The Electrochemical Society. Presentation of the medal and $1000 prize will be made at the banquet to be held on October 2, 1956, in conjunction with the Cleveland Meeting of the Society. The Award is made for conspicuous "contribution to the advancement of the objects, purposes, or activities" of the Society.

Dr. Burns has served as Society Treasurer, Secretary, and President, and at present is Chairman of its Publication Committee and the Editorial Staff of the JOURNAL.

He is a graduate of the University of Colorado which later conferred on him the honorary degree Doctor of Science. His graduate work at Princeton University led to the Ph.D. degree in 1921. He was elected to membership in the Colorado University Chapters of Phi Beta Kappa, Sigma Xi, and Tau Beta Pi. His social fraternity is Delta Tau Delta and he has been national president of Alpha Chi Sigma, the professional chemical fraternity. Dr. Burns has long been a member of the American Chemical Society and has been chairman of its New York Section.

©Fabian Bachrach

R. M. BURNS

He was awarded the 1952 Perkin Medal for achievement in American industrial chemistry, and the 1953 Willis Rodney Whitney Award of the National Association of Corrosion Engineers. He is a member of the Technical Advisory Panel on Biological and Chemical Warfare to the Assistant Secretary of Defense for Research and Development, the Advisory Committee to the Department of Chemistry at Princeton University, the Advisory Committee to the Research Division of the College of Engineering of New York University, the Society of Chemical Industry, and the American Association for the Advancement of Science.

In World War I, he served in the Chemical Warfare Service. After a year as research chemist with the Barrett Co., he became a member of the technical staff of the Western Electric Co. and later of the Bell Telephone Labs. upon its organization in 1925.

Dr. Burns has published numerous papers in the field of corrosion. He is senior author of the book "Protective Coatings for Metals."

Since his retirement from Bell Labs., he has been a Scientific Advisor to Stanford Research Institute at Menlo Park, Calif., and to Sprague Electric Co., North Adams, Mass.

His avocations are book collecting, gardening, walking, skiing, and mountain climbing. He has been president of the New York Section of the Green Mountain Club and chairman of the New York Chapter of the Appalachian Mountain Club. He lives with his wife and daughter, Nadja, in Summit, N. J.

Further Plans for Cleveland Meeting

Arrangements for the fall meeting of the Society in Cleveland, September 30–October 4, are rapidly nearing completion. The complete program, including general information, technical sessions, and abstracts, will appear in the September JOURNAL.

Reservations

Members will soon receive hotel reservation cards, together with a letter listing hotels, motels, and eating places in Cleveland. When making reservation requests, which should be sent directly to the hotel, please be sure to mention The Electrochemical Society.

Technical Program

The Battery Division has planned six sessions, two of which are joint with the Theoretical Electrochemistry Division. The Corrosion Division also has six sessions. The Electrodeposition Division has scheduled one session of general interest and three joint with the Theoretical Division. Electrothermics and Metallurgy and Electronics—Semiconductors are scheduled for four sessions.

Special Symposia

In addition to general symposia, the Battery Division has scheduled a symposium on the Life of Automotive Batteries and symposia on Electrode Polarization jointly with the Theoretical Electrochemistry Division. The Corrosion Division plans symposia on High Temperature Oxidation, Factors Related to Corrosion, Corrosion Kinetics, and the Electrochemistry of Corrosion. The Electrothermics and Metallurgy Division has scheduled symposia on Acheson Furnaces, Processes, Products, and Related Developments, and on New Chemical Developments in the Extractive Metallurgy of Titanium. The Electronics—Semiconductor papers will be of the late-news type.

Ladies' Program

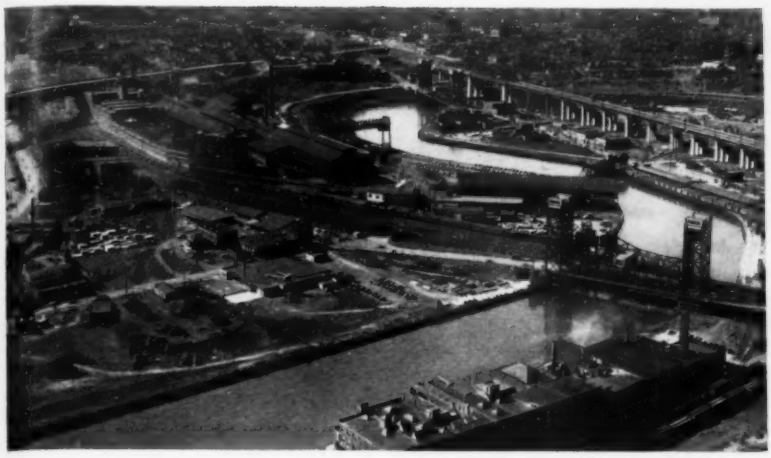
A Ladies' Program that promises to be a real social success is being organized by Mrs. M. Korver and the other members of the ladies' committee.

Plant Trips

A trip is scheduled to Western Reserve University and Case Institute of Technology, for inspection of facilities and research activities.

Also planned are visits to the new National Carbon Research Lab. in Parma, and to the General Electric Lighting Institute, located at the Lamp Division headquarters in Nela Park, Cleveland.

The primary purpose of the Lighting Institute is education. Its displays and facilities are for training all segments of



Cleveland's industrial area, showing the muddy, winding Cuyahoga River and the huge industrial plants in the city's "industrial valley" situated immediately behind the downtown area.

the lighting industry and its customers in the techniques and values of good lighting practice. It is a contemporary, dynamic, and commercial training facility. The "Institute" idea of lighting demonstration and education was originated at Nela Park in 1919. In 1923, the Nela School of Lighting was established with permanent space provided in the basement of the Advertising Bldg. In the same year, the General Electric Lighting Institute was developed in its present building. This structure is used exclusively for Lighting Institute purposes.

The Institute is a part of the marketing organization of the Lamp Division. It sponsors courses and conferences which provide lighting applications and lighting sales training to contractors, distributors, and electric utility representatives. In addition, there are lamp and lighting training courses and conferences for industrial, school, store, office, and residential customers, as well as architects and consulting engineers in these fields.

One week each year the Institute concentrates on vocational guidance activities. The week in which Thomas A. Edison's birthday falls each February is designated as Edison Science Week. Members of the Institute staff not only show how Mr. Edison constructed his first practical incandescent lamp, but demonstrate good contemporary lighting effects to the members of visiting high school classes. It is an excellent opportunity for the Institute to present to the students a close look at a particular branch of the electrical industry, and also the chance to encourage their following science and engineering careers.

Now, more than ever, there is a need for lighting education in all fields of American business, industry, and life. To help provide this education, the Lighting Institute is continually revising its facilities and keeping its courses up-to-date on the latest techniques. But, most important, it is telling the lighting story to more and more people every day. It will continue to do this in the future.

Highlights of the Meeting of the Board of Directors

(Held April 29, 1956, Hotel Mark Hopkins, San Francisco, Calif.)

Communications from the President

The President reported that the Deutsch Bunsengesellschaft has voted to cooperate with The Electrochemical Society in sponsoring a Conference on Passivity.

A letter from Dr. T. L. Rama Char, Secretary-Treasurer of the India Section, thanking the Society for obtaining support from the Asia Foundation to help Indian members with dues, was read by the President.

The President announced that the following members had been appointed and had agreed to serve on the Investment Advisory Panel: George W. Heise, Chairman, Clyde Williams, A. K. Graham. These appointments were approved.

Communications from the Treasurer

The Treasurer's Report was published in the July JOURNAL, p. 148C.

Communications from the Secretary

The Secretary presented the Report of the Audit of the Society's funds for the last fiscal year. This report was published in the July JOURNAL, p. 149C.

The Secretary announced that, according to the Constitution, Article IX, Section 3, the fiscal year of the Society shall start January 1. On motion of Dr. Burns, it was voted that the fiscal year of the Society would be changed from January 1–December 31 to April 1–March 31, effective this year, and that the Constitution and Bylaws Committee be authorized immediately to prepare a revision of the Constitution in conformity with this action.

The Secretary then presented the following budget, which is to operate for the period January 1, 1956 to March 31, 1957. On motion of Dr. Gilbertson, this budget was approved with one revision, namely, increasing the budgeted amount for the printing and mailing of the JOURNAL.

The Secretary announced that the International Nickel Co. had become our first Patron Member.

On motion of Dr. Burns it was voted that the Southern California-Nevada Section be chartered with the following officers: Thomas Blair, Chairman; William Hetherington, Vice-Chairman; Lee J. Droege, Secretary-Treasurer.

The Bylaws of the Boston Section were approved as distributed.

The Secretary announced that the Cleveland Section had awarded Student Associate Memberships, as has been its practice of late. The following have been so honored: Robert Edwin Hagman, Case Institute of Technology; Stewart J. Strickler, College of Wooster; James J. Zwolenik, Western Reserve Uni-

versity; Lewis M. Elton, Fenn College; Ora Ferguson, Hiram College.

Report of Council of Local Sections

This report was presented by F. W. Koerker, Chairman. The Council of Local Sections has been very active this past year and was instrumental in chartering the Boston and Southern California-Nevada Sections. Furthermore, as stated in the report, the following areas are now working on forming a Section: Milwaukee-Madison, Houston, Indianapolis, St. Louis, Central New York, Baton Rouge-New Orleans.

Ways and Means Committee

The Ways and Means Committee had recommended several changes in Bylaws. The Bylaws, as revised, appear on p. 172C of this issue.

Furthermore, the Committee recommended a change in the Constitution, Article II, Section 9, to revise the qualifications for Emeritus membership. These changes will be started through the regular procedure for a change in Constitution.

At the recommendation of the Committee, the authority of the Assistant Secretary has been formalized as follows: "The Assistant Secretary shall be responsible only to the Secretary."

The Committee recommended that, in the light of the change in the A.A.A.S. representation, we should be represented in Section B—Physics, Section M—Engineering, Section P—Industrial Science, in addition to Section C—Chemistry, as in the past.

The Committee recommended that the representation of Sustaining Members and Patrons be formalized in the Bylaws along the following lines. Patrons shall be allowed two representatives—one representing the technical level and one the managerial level of the company. They shall be eligible to receive, on request, up to ten subscriptions to the JOURNAL and/or bound volumes for their libraries. Sustaining Members with one membership shall have one representative and receive one subscription to the JOURNAL and/or one bound volume. Companies holding multiple Sustaining memberships shall have two representatives, and two only, regardless of the number of memberships held. One shall be a representative of management and one at the technical level, and they shall receive, on request, the number of subscriptions to the JOURNAL as represented by the number of Sustaining memberships for their libraries. Further, any Sustaining Member representative otherwise eligible for membership in The Electrochemical Society shall be considered an Active Member of the Society.

At the recommendation of the Ways and Means Committee, the Board voted to appoint a Resolutions Committee.

Furthermore, as a recommendation of the Ways and Means Committee, as many other funds of the Society as possible should be invested as a unit by the Finance Committee upon the recommendation of the Investment Advisory Panel.

PROPOSED BUDGET 1/1/56–3/31/57

Income

	Estimated Value	Budget Approved 1/27/56 for Fiscal Year 1/1/56-12/31/56
Membership Dues	$40,750	$32,600
Sustaining Memberships	15,000	12,000
Reprints	5,000	4,000
Nonmember Journal Subscriptions	27,500	22,000
Office Sale Journal & Publications	1,250	1,000
Conventions	5,000	5,000
Advertising	17,500	14,000
Bound Volumes	2,000	2,000
Membership Directory	400	—
Income for General Reserve:		
Nonmember Journal Subscriptions	5,440	4,350
Nonmember Convention Registrations	1,200	1,200
Monograph Royalties	1,560	1,250
Total	$122,600	$99,400

Expenses

Printing & Mailing Journal	$44,750	$31,000
Reprints	3,120	2,250
Publication Committee	440	350
Advertising Commission	6,500	5,200
Salaries, Social Security, & Insurance	46,750	37,400
Rent	4,400	3,600
Postage, Supplies, & Miscellaneous	7,715	6,175
Local Sections & Divisions	1,250	1,000
Young Author's Prize	100	100
Reserve for Office Equipment	731	585
Bound Volumes	2,000	2,000
Membership Directory	750	—
Convention Expenses Less Salary Charges:		
Program Booklet	1,380	1,380
Travel of N. Y. Personnel	1,500	1,500
Materials & Supplies	320	320
Postage & Express	490	490
Total	$122,196	$93,600
Excess Income Over Expenditures	$404	$5,800

Report of Finance Committee

The Finance Committee reported that (*a*) the various funds derived from monographs be labeled "Corrosion Division Monograph Fund," "Electrodeposition Division Monograph Fund," etc., rather than "Modern Electroplating Fund" or "Corrosion Handbook Fund," etc.; (*b*) each Division sponsoring monographs should appoint an active committee to make recommendations on expenditures from these funds; (*c*) the income from investment of the various divisional monograph funds should be added to our Society Reserve Fund. On motion of Dr. Gilbertson, these three recommendations were accepted.

Report of Publication Committee

JOURNAL Statistics as of April 9 are:

Manuscripts

Published (including May issue)	56

Accepted and awaiting publication	40
Under review or revision	90
Rejected since January 1, 1956	10
Pages Published (including May)	
Technical papers, notes, and reviews	303
Current affairs, editorials, and ads	126
Total	429
Budget	$31,000

Printing Costs

Month	Total Costs	Pages	Cost/Page
January	4015	110	36.50
February	3210	94	34.14
March	2848	85*	33.50

The budget will require that the remaining nine issues of the JOURNAL for 1956 be printed at an average cost of $2325 per issue. This will permit issues of about 64 pages, of which 48 pages can be devoted to Technical Papers.

The Technical Editor and his staff are insisting upon extreme brevity and conciseness (with increasing lamentation from authors) but, even so, original papers average almost six pages each. Using smaller type and running one article directly after another permits the publication of a few more papers during the year, but the page cost is increased by increased composition cost.

As of April 9, accepted manuscripts on hand were sufficient for the June, July, August, and September issues. The prospect is for an increasing backlog of papers and longer delay in publication. It is to be hoped that further funds for publication will be available later in the year.

Monograph Statistics

Sales of Publications

"Corrosion Handbook," Uhlig, 1948: 1948—6224; 1949—1683; 1950—1272; 1951—1104; 1952—1109; 1953—927; 1954—1097; 1955—959; 1956—253. Total—14,628.

"Modern Electroplating," Gray, 1953: 1953—965; 1954—2631; 1955—817; 1956—182. Total—4595.

"Vapor-Plating," Powell, Campbell, and Gonser, 1955: 1955—1405; 1956—117. Total—1211.

"Electrochemistry in Biology and Medicine," Shedlovsky, 1955: 1955—1015; 1956—196. Total—1211.

"High Temperature Technology," Campbell, 1956: 1956—464.

"Abstracts of the Literature on Semiconducting and Luminescent Materials," Battelle Memorial Institute. 1953 Issue published 1955: 1955—887; 1956—77. Total—964. 1954 Issue published 1955: 1955—382; 1956—362. Total—744.

Books Under Consideration and Under Contract

"Abstracts of the Literature on Semiconducting and Luminescent Materials"—Manuscript for the 1955 issue is due to be delivered in the fall.

"Corrosion Handbook," 2nd Ed.—Some years off.

"Electro-Organic Chemistry"—The organization of this project awaits the completion of Dr. S. Swann's bibliography.

"Rare Metals"—This is a good possibility, about which we have had no recent word.

"Stress Corrosion Phenomena," W. D. Robertson, Editor—This is in process.

"Theoretical Electrochemistry" and "Industrial Electrochemistry"—Both prospects have been discussed generally with Dr. J. C. Warner of Carnegie Tech who feels cooperation is essential. Both books would, of course, be well received.

(Signed) R. M. BURNS, *Chairman*

After reports of representatives of other standing committees of the Society, Dr. Uhlig turned the meeting over to President-Elect Hans Thurnauer to make committee appointments for the coming year. These appointments were as follows:

Admissions Committee—L. Weisberg, Chairman; L. I. Gilbertson and M. F. Quaely.

Corrosion Handbook Committee—N. Hackerman added as a member.

Finance Committee—L. I. Gilbertson, Chairman; H. B. Linford, R. A. Schaefer, W. C. Gardiner, and S. Swann, Jr.

Membership Committee—F. W. Koerker, Chairman.

Nominating Committee—R. M. Burns, Chairman; W. Duckworth, H. M. Scholberg, A. E. Middleton, and M. J. Udy.

Perkin Medal Committee—President H. Thurnauer, Chairman; N. Hackerman and H. H. Uhlig, members; F. A. Lowenheim, L. I. Gilbertson, and C. V. King, alternates.

Publication Committee—R. M. Burns, Chairman; H. B. Linford and N. Hackerman.

Sustaining Membership Committee—F. L. LaQue, Chairman. Members to be selected by Chairman.

Ways and Means Committee—S. Swann, Jr., Chairman; G. W. Heise, F. A. Lowenheim, N. Hackerman, W. C. Gardiner, H. H. Uhlig, and R. A. Schaefer.

Publicity Committee—None.

Representatives in different societies—Remain same as at present. However, due to the death of C. C. Rose, W. J. Hamer of the National Bureau of Standards was appointed to fill vacancy on Committees C-40, C-18, C-10, and C-42.

Committee on Resolutions—R. M. Burns, Chairman; H. B. Linford and William Blum.

Becket Award Committee—Remain same (I. E. Campbell, Chairman; J. H. Brennan and A. T. Hinckley) until one of the awards is on the way.

Acheson Medal Award Committee (to be appointed next fall)—G. W. Heise, Chairman; R. M. Hunter and E. M. Sherwood.

On motion of Dr. Hackerman, these appointments were approved.

The Secretary then submitted his customary resignation and absented himself from the room to allow the Board to reach an independent decision upon continuation. The Board requested that the Secretary continue as in the past.

The meeting was adjourned at 6 P.M.

HENRY B. LINFORD, *Secretary*

DIVISION NEWS

Battery Division

The Nominating Committee of the Battery Division, E. Willihnganz, W. Hamer, and K. Willson, has nominated the following for officers of the Division:

Chairman—U. B. Thomas

Vice-Chairman—J. C. White

Secretary-Treasurer—E. J. Ritchie

Executive Committee (2 of following to be elected)—W. S. Herbert, C. K. Morehouse, J. J. Coleman, and M. Lang

Additional nominations may be made either in writing to the Division Chairman or from the floor, providing the

(*Continued on page 175C*)

* This issue had a total of 100 pages, 15 of which were devoted to abstracts of papers for the San Francisco Meeting and charged to this meeting.

Bylaws of The Electrochemical Society, Inc.

(As Approved at the Board of Directors' Meeting, April 29, 1956)

Article I

Order of Business

Section 1. At the annual business meeting of the Society, the order of procedure shall be as follows:

Approval of the minutes of last meeting.
Report of the Board of Directors, including those of the Secretary and the Treasurer.
Reports of Standing Committees.
Deferred Business.
New Business.
Report of Tellers of election.
Address of the retiring President. (This may be presented at another session of the general meeting, at the discretion of the framers of the program of the meeting.)

Section 2. The annual business meeting of the Society shall preferably be on the second day of the general meeting.

Article II

Meetings of the Board of Directors

Section 1. The Board of Directors shall hold a regular meeting immediately preceding each general meeting of the Society.

Section 2. Between said meetings the Board of Directors may hold special meetings when called by the President.

Section 3. All meetings of the Board of Directors shall be open to Past Presidents. The President shall have the authority to invite persons to attend meetings of the Board of Directors, who will in his judgment be of assistance to the Board in the transaction of its business.

Section 4. At the regular meetings of the Board of Directors, the order of procedure shall be as follows:

Approval of the minutes of the last regular meeting and of any special meeting the minutes of which have not been approved.
Appointment of tellers of election.
Communications from the President.
Communications from the Treasurer.
Communications from the Secretary.
Discussion of programs of future meetings of the Society.
Reports of Committees.
Deferred business.
New business.
Adjournment.

Section 5. At special meetings of the Board of Directors, the order of procedure shall include the approval of the minutes of the past meeting of the Board and such other of the above items of procedure in their order given as are to be acted upon.

Article III

Duties of Officers

Section 1. The President shall preside at all business meetings of the Society and at those of the Board of Directors. He may represent the Society at any function to which no other particular delegate has been appointed by the Society or the Board of Directors.

Section 2. The Secretary, besides performing the usual duties of that office, shall be the guardian of the records of the Society, collect dues from members, and all bills owing to the Society, and pay such amounts to the Treasurer. He shall report to the Board of Directors at each of its meetings on the condition of the affairs of the Society and make such recommendations as he thinks will facilitate the transaction of the business affairs of the Society or in any way advance its interests.

Section 3. The Treasurer shall report to the Board of Directors at its meeting immediately preceding the business session of the annual meeting of the Society on the condition of the finances of the Society and make such recommendations as will in his opinion tend to safeguard or improve the same.

Section 4. The Board of Directors shall report to the annual meeting on the general affairs of the Society, including the abstracts of the reports of the Secretary and Treasurer and any other matters which they may consider of interest to the Society.

Section 5. All funds of the Society shall be disbursed on checks signed jointly by the Secretary and Treasurer of the Society, or their agents as authorized by the Board of Directors. For disbursal of regular expenditures they may establish agents funds which are under the control of the Secretary.

Article IV

Publication Committee

Section 1. A Publication Committee of three members shall be appointed annually by the Board of Directors. Its Chairman shall be the Editor of all publications of the Society. A second member, called the Technical Editor, shall supervise review of papers submitted for publication. A third member, called the Business Manager, shall handle the financial and business matters of publication. The Publication Committee shall recommend to the Board of Directors the scope and field of activities of the Society's publications.

Section 2. A Committee of Divisional Editors shall be selected by the Chairman of the Publication Committee, subject to the approval of the Board of Directors. This Committee shall consist of at least one representative of each Division of the Society. The Technical Editor shall be Chairman of the Committee of Divisional Editors which shall jointly arrange review of all papers submitted. It shall make recommendations to the Publication Committee concerning acceptance of papers for publication. The Publication Committee shall render a decision on papers as promptly as possible and shall, as occasion permits, assist authors to meet publication standards of the Society.

Section 3. The Publication Committee shall have charge of the publication of the Journal of the Society and shall decide what papers shall be published in the Journal. It shall set final dates for submission of papers and shall establish standards of quality, subject to further provisions of these Bylaws, and to the wishes of the Board of Directors. It shall publish in the Journal such other editorial material and news as it, and the Board of Directors, may deem desirable.

The Chairman of the Publication Committee shall appoint an adequate editorial staff for the Journal, the positions and the appointees to be subject to the approval of the Board of Directors.

Article V

Programs

Papers, abstracts, reports, and any material given at the technical sessions of the Society shall be assembled by the joint action of the Officers of the Divisions and the Secretary of the Society. Such papers, abstracts, and reports may be solicited by any of them. The Secretary shall set the date deadline for their inclusion in the technical program, and with the Division Officers shall give or refuse permission for presentation, except that any paper already accepted for publication in the Journal cannot be refused.

Article VI

Appeals

Appeals from decisions of the Secretary, Publication Committee, or Division Officers may be made in writing by any member to the Board of Directors which

has the power to alter or confirm the appealed decision.

Article VII

PUBLICATIONS OF THE SOCIETY

Section 1. Effective January 1, 1948, there is established a monthly publication of the Society to be called "Journal of The Electrochemical Society."

Section 2. The Journal shall contain such technical articles and other additional material as the Publication Committee, which is established in Article IV of these Bylaws, shall determine to publish.

Section 3. Each year the Board of Directors shall, upon the advice of the Finance Committee, set up a budget to cover all expenses of the Journal. The Publication Committee shall operate the Journal within this budget, subject to a review of its operation at each and every meeting of the Board of Directors. Warrants for the payment of bills from the fund thus set up shall be signed by the President and Business Manager and shall be disbursed from the funds of the Society by the officers empowered to disburse the Society funds.

All income to the Journal from advertising and sales of subscriptions shall be received into the General Fund of the Society by the Secretary and Treasurer.

Article VIII

STANDING AND SPECIAL COMMITTEES

Section 1. The following Standing Committees shall be maintained in addition to the Admissions Committee established under Article III, Section 3, of the Constitution: Ways and Means, Finance, Membership, Sustaining Membership, Acheson Medal Award, and Palladium.

Section 2. The President may appoint special committees to conduct investigations or to represent the Society on special occasions.

Section 3. Unless otherwise specified, all committee appointments shall expire with the term of the President who made the appointments.

Section 4. Each Committee shall submit an annual written report to the Board of Directors of its activities.

Article IX

WAYS AND MEANS COMMITTEE

Section 1. The Ways and Means Committee shall act as an advisory group to the President and Board of Directors on all phases of the Society's business.

Section 2. The ways and Means Committee shall be composed of seven members. The Chairman of this Committee shall be appointed from among the Board of Directors, and it shall include one Vice-President and at least two Past Presidents of the Society. The members of this Committee shall be appointed by the President immediately upon assuming office.

Section 3. The Ways and Means Committee may carry on its business through subcommittees composed of a Chairman, who shall always be a member of the Committee, and such other members of the Society at large as the Chairman of such subcommittees may select.

Section 4. The Ways and Means Committee shall have the power to call on any of the officers of the Society or of its Sections or Divisions to furnish this Committee with such information as it may deem necessary competently to advise the President and Board of Directors as to policies to be followed in the conduct of the Society's affairs.

Section 5. The Ways and Means Committee shall report at appropriate intervals to the President and Board of Directors upon such items of the Society's business as have been referred to this Committee for attention.

Article X

FINANCE

Section 1. The Finance Committee shall consist of five members. The Finance Committee shall assist the Board of Directors in the preparation of a budget and advise the Board on matters of income, expense, and investment of all funds and all other financial operations of the Society.

Section 2. The Finance Committee shall submit a budget to the Board not later than January 15 of the year for which it is to apply. The Committee shall review at each meeting of the Board the operations of the Society and report to the Board its findings.

Section 3. The Committee shall be composed of the following and be appointed by the President: the Treasurer, the Secretary, the Business Manager of the Journal, a Vice-President, and the Chairman of the Ways and Means Committee, unless he holds one of the aforesaid offices, in which event any member of the Society may be appointed in his stead.

Section 4. The Finance Committee shall recommend annually to the Board of Directors a policy of investment of the principal and the allocation of monies which have accumulated in the General Fund of the Society, or in any of the Special Funds under its control.

Article XI

MEMBERSHIP COMMITTEE

Section 1. The Committee on Membership shall maintain a continuing program for the enlargement of the membership of the Society.

Section 2. Each Division and Local Section of the Society shall submit annually to the President the names of two of its members as nominees for the Membership Committee, and the President shall, with the approval of the Board of Directors, select one of the persons so proposed as the representative of his Division or Local Section on the Membership Committee.

Section 3. The President shall, in addition, subject to the approval of the Board of Directors, appoint an additional member of the Committee to serve as Chairman of the Membership Committee.

Article XII

ACHESON AND PALLADIUM MEDAL AWARDS

The Acheson Medal Award shall be made by the Board of Directors upon the recommendation of the Acheson Award Committee. The Committee shall function in accordance with the rules accepted and approved by the Board of Directors, March 3, 1949.

The Palladium Medal shall be awarded by the Palladium Medal Award Committee which shall be selected and which shall function in accordance with the rules and regulations approved by the Board of Directors on October 9, 1955.

Article XIII

ACCOUNTS OF THE SOCIETY

The Board of Directors shall engage a public accountant, not later than December 15th each year, to audit the current accounts and financial statements of the Secretary and Treasurer of the Society. The report of such accountant shall be submitted in such form as to designate the source of all receipts by the Society and the disposition of all funds expended. It shall also include, as far as possible, a statement of the assets and liabilities of the Society so drawn up as to show clearly the net worth of the Society as of December 31st of the year for which the audit is made. The report of the auditor shall be submitted to the Board of Directors through the Treasurer of the Society.

This report shall be printed in the Society's Journal not later than two months after its approval by the Board.

The general results of this audit shall be reported to the members of the Society at the Annual Meeting.

Article XIV

GUESTS AT MEETINGS

Nonmembers may attend technical meetings and social functions of the Society. Requirements for registration of nonmembers may be established by the Local Committee in charge of said functions.

Article XV

SESSION ON ELECTROTHERMICS

At least one session at one general meeting of the Society each year shall be

devoted to the subject of Electrothermics.

Article XVI

Divisions

Section 1. Any member of the Society may register for membership in any Division in which he is interested and may resign therefrom at his discretion.

Section 2. The Officers of the Division shall be a Chairman, one or more Vice-Chairmen, and a Secretary and a Treasurer. The Offices of Secretary and Treasurer may be held by the same person. The above officers, together with two or more members of the Division, shall constitute the Executive Committee of the Division.

The Division shall elect its officers and other members of the Executive Committee during a general meeting of the Society or within thirty days thereafter. The officers and other committee members shall be elected for such terms as the Division Bylaws provide, these terms of office not to exceed two years. An officer may be re-elected, however, if the Division Bylaws do not prohibit such re-election.

Section 3. A Division shall hold, if possible, one session a year at a general meeting of the Society, such session to be under the auspices of said Division, and publication of papers for such sessions to be subject to the usual regulations and control of the Publication Committee.

Section 4. The Society shall not be responsible for any debts contracted by the Divisions or by the officers thereof. Divisions may receive from the Society such financial assistance as the Board of Directors may determine to be proper, provided such request is accompanied by a financial statement covering the previous fiscal year. It is recommended that each Division submit a financial report within three months of the close of its fiscal year. Such funds shall be used for sending out notices, for solicitation of papers, and for the legitimate work of the Divisions.

Section 5. The Board of Directors may recommend the dissolution of any Division of the Society, such recommendation to be submitted to a vote of the members present at an annual business meeting of the Society.

Section 6. Divisions shall have the privilege of suggesting to the Secretary the names of eligible candidates for officers of the Society. Such suggestions shall be in the hands of the Nominating Committee prior to April 1 each year. The Secretary shall transmit such suggestions to the Chairman of the Nominating Committee when he has been selected.

Section 7. It shall be the duty of the Secretary of the Society to call to the attention of the officers of each Division all of the provisions of Article VIII at least once between January 1st and April 1st each year.

Article XVII

Regulations Concerning the Formation and Conduct of Local Sections

Section 1. Geographic boundaries of the several Local Sections shall be set from time to time by the Board of Directors upon the advice of the Council of Local Sections. Members of the Society living or having their principal place of business within said boundaries shall be members of the appropriate Local Section, provided they comply with the regulations of the said Section. Members of the Society may become affiliated with any Section upon application to the Secretary of that Section. Only members of this Society are eligible for membership in the Local Sections.

Section 2. The following provisions shall apply to financial matters of common interest to the Local Section and the Society: (1) The expenses of each Local Section shall be borne by the members enrolled in said Section. The Society shall not be responsible for any debts contracted by a Local Section or by the Officers thereof. Exceptions can be made only in the case of General Meetings for which the Local Section acts as host, as provided in Section 5. (2) Local Sections submitting proof of at least three technical meetings during the fiscal year of the Society will thereupon be granted a sum of fifty dollars each as financial assistance.

Additional financial assistance up to fifty cents per member may be provided by the Society in each fiscal year, provided the Local Section raises an equal amount from local dues, assessments, or transfer of funds from inactive accounts. Such additional assistance will be made only upon written request of the Local Section, accompanied by a financial statement. This financial statement is due within three months of the close of the fiscal year of the Section. Funds received by Local Sections from the Society as provided herein shall be used solely for the rent of meeting rooms, sending out notices, and paying expenses of persons invited to speak before such Local Sections. (3) Local Sections will receive one dollar from the initial dues of a new member, such sum to be sent to the Local Section by the Secretary of the Society, provided the Local Section was active in securing said new members. To obtain credit for new members, the application must be forwarded to the Secretary of the Society by the Secretary of the Local Section.

Section 3. Papers read before Local Sections, and discussions thereon, if reported, are to be considered as the property of this Society. The Society shall have the first right to publish such papers. Reading of a paper before a Local Section does not carry with it the right of publication in the Journal.

Papers read before Local Sections may be offered for reading at general meetings of the Society, and will be given equal standing with other papers on the program of said meeting, when approved by the Publication Committee.

Section 4. Each Local Section shall transmit promptly after each meeting, to the Secretary of the Society, an abstract of its proceedings, including the titles and names of authors of all papers read before it, for the purpose of preparing a report to the Board of Directors, and for the purpose of enabling the Board of Directors to comply with Section 3.

Section 5. When a Local Section acts as host for a General Meeting of the Society, it shall elect one of the following two plans for handling finances of such meetings and shall so advise the Secretary of the Society not less than 90 days prior to the opening of such meeting.

Plan A. The Local Section assumes full responsibility for handling finances of the General Meeting, is responsible for all debts, and may retain any surplus, after paying to the Society a head tax on registrants as determined by the Board of Directors, and provided further that the expenditures of any surplus retained by the Local Section shall be subject to the general approval of the Board of Directors. Local Sections shall submit a complete financial report to the Secretary of the Society as soon as possible after the close of the meeting and in case of a deficit shall notify the Secretary when said deficit has been discharged.

Plan B. The Local Section assists the Board of Directors and the Secretary of the Society in handling the finances of the meeting in its territory, but makes no financial arrangements without the general approval of the Secretary of the Society; the Society shall be responsible for any deficit and shall retain any surplus.

Section 6. Upon the request of a Local Section, the Secretary will endeavor to arrange for an outstanding speaker to visit such Section, provided the Section will accommodate its meeting date to whatever extent is necessary. The Local Section will be responsible for local expenses of the speaker while he is in their city. Suggestions as to preferred speakers will be welcomed by the Secretary of the Society.

Section 7. Prior to July 1st each year, each Section shall appoint or elect a Councilor to the Council of Local Sections. Such Councilor shall be an active member in good standing in the Society and shall hold office for two years, beginning on July 1st immediately following his or her election, and each Section shall be entitled to two such Councilors. In addition, members of the

Society not attached to any Local Section may be placed on the Council by petition of ten members of the Society. Not more than two such Councilors-at-Large may hold office at any one time. Such Councilors-at-Large cannot be from any one locality for more than one two-year term in succession unless a Local Section has been formed in the interim and they thus become regular councilors.

Section 8. The Council of Local Sections shall hold a meeting at each general meeting of the Society. The duties of the Council of Local Sections shall be: (1) to consider problems affecting the welfare and operation of the Local Sections and to work toward their solutions, (2) to act as a clearing house on information, problems, and methods of organization of Local Sections, (3) to act as an advisory council to the Board of Directors of the Society on Local Section affairs, and (4) to make recommendations to the Board of Directors on such other matters relating to the interests of the individual members of the Society as the Councilors may become aware of from time to time.

Section 9. The Council of Local Sections shall elect one of its Local Section Councilors to the Board of Directors at each Spring Meeting of the Council, for a two-year term, and he will be seated immediately at the next meeting of the Board of Directors. During the period a Councilor is a member of the Board of Directors he shall continue to be a member of the Council. The Council shall also elect a Chairman, Vice-Chairman, and Secretary from its Local Section Councilors to conduct the necessary meetings and correspondence of the Council. A set of Bylaws will be adopted for approval of the Board of Directors to guide the formation and operation of the Council.

Section 10. Local Sections shall have the privilege of suggesting to the Secretary the names of eligible candidates for officers of the Society. Such suggestions shall be in the hands of the Nominating Committee prior to April 1 each year. The Secretary shall transmit such suggestions to the Chairman of the Nominating Committee when he has been selected.

Section 11. It shall be the duty of the Secretary of the Society to call to the attention of the officers of each Local Section all of the provisions of Article XVII at least once between January 1st and April 1st each year.

Article XVIII

DUES AND FEES

Section 1. The annual dues for Active Members shall be fifteen dollars, of which five dollars shall be a nondeductible subscription to the Journal of The Electrochemical Society. The annual dues for Student Associate Members shall be three dollars, and for Associate Members nine and a half dollars. Each Student Associate Member and each Associate Member shall receive the Journal of The Electrochemical Society. The subscription price of the Journal of The Electrochemical Society to nonmembers shall be set annually before November 1 by the Board of Directors.

Section 2. Any Active Member of the Society may become a Life member upon payment of a life membership fee of $300 which shall entitle the Life Member to a life subscription to the Journal and shall relieve said Life Member of the future payment of annual dues.

Section 3. Annual dues of Sustaining Members shall be $100 or more. Those Sustaining Members that contribute at least $1,000 a year to the Society shall be designated as Patrons.

Section 4. Emeritus Members shall be exempt from the payment of annual dues and shall receive the Journal of The Electrochemical Society without charge.

Section 5. Society Divisions and Local Sections may collect Division or Section dues as authorized by their respective Bylaws.

Article XIX

AMENDMENTS

Amendment to these Bylaws may be proposed by the Board of Directors and shall require a two-thirds vote of the whole Board for their adoption; proxy and mail votes shall be counted when received before the vote is counted. The text of the proposed amendments shall be transmitted to each member of the Board of Directors at least ten days before the meeting at which the vote on the same is to be taken.

Division News

(*Continued from page 171C*)

nominee's willingness to serve, if elected, has been assured.

Officers will be elected at the Division's luncheon and business meeting, Tuesday, October 2, in Cleveland.

Electro-Organic Division

The Nominating Committee of the Division has proposed Dr. Milton Allen as the new Secretary. The election will be held at the fall meeting of the Society in Cleveland.

Any further suggestions will be welcomed. These should be sent to the Committee Chairman, Dr. Christopher L. Wilson, Hudson Foam Plastics Corp., Lake Ave. & Saw Mill River Rd., Yonkers 2, N. Y.

Electrothermics and Metallurgy Division

At San Francisco, on May 2, the Division had its annual luncheon-business meeting in the Fairmont Hotel. The Chairman presented a brief summary of the Treasurer's Report and an informal progress report.

Two symposia have been organized for the Cleveland Meeting. Tentatively, only one symposium, dealing with new forms of energy, has been proposed for the Washington Meeting, for which a chairman is needed. Suggestions of additional subjects are requested. The single symposium planned thus far for the Buffalo Meeting is entitled "Electric Furnace Ferroalloys and Slags."

Mr. Gary Steven, Armour Research Foundation, has resigned as Member-at-Large. Mr. W. E. Kuhn, The Carborundum Co., has been appointed to the vacancy.

A brief report of the Becket Memorial Award was presented.

Word from the National Safety Council indicates that the data sheet on the safe handling of zirconium powder will be available by late summer or early fall. This is a direct result of a Society committee of about two years ago in which the E & M Division played an active part.

The highlight of the meeting was a most excellent and enjoyable talk on San Francisco and its surrounding areas given by Mr. Lloyd Graybiel, Vice-President of the American Trust Co.

A. C. HASKELL, JR., *Chairman*

Industrial Electrolytic Division

At the annual business meeting of the Division, held in San Francisco, the following officers were elected for two-year terms:

Chairman—Milton Janes
Vice-Chairman—J. C. Cole
Secretary-Treasurer—Warren D. Sherrow, Great Lakes Carbon Corp., Hancock Bldg., Niagara Falls, N. Y.

The highlight of the business meeting was the presentation by Dr. W. C. Gardiner of the annual "Report of the Chlor-Alkali Committee" for 1955, prepared by W. C. Gardiner, M. S.

Kircher, and W. D. Sherrow. This report will be published in the September JOURNAL.

The Division is planning to hold symposia at the Washington Meeting, May 12–16, 1957, and will welcome contributions as early as possible.

M. JANES, *Chairman*

Theoretical Electrochemistry Division

On May 3, the Theoretical Division held its annual business meeting in San Francisco with Ernest Yeager, Chairman of the Division, presiding. Approximately 75 people attended the business meeting.

Plans were presented with respect to the activities of the Division for the meeting in Cleveland, September 1956, and the meeting in Washington, May 1957.

For the first time at a fall meeting, general sessions will be scheduled at Cleveland for the Theoretical Division. This action is the result of the increase in the number of contributed papers as well as a reluctance to decrease the time available for each paper.

In May 1957, the Theoretical Division will sponsor a symposium on electrolytes with Dr. Walter Hamer of the National Bureau of Standards presiding. This symposium will be concerned with aqueous and nonaqueous systems. It is hoped that a monograph on electrolytes can be prepared in conjunction with this symposium.

An attempt will be made to prepare combined extended abstract booklets for several Divisions for the first time at the Cleveland Meeting.

A committee will be appointed to consider the establishment of a program of graduate and postdoctorate fellowships in electrochemistry as suggested by Dr. J. O'M. Bockris of the University of Pennsylvania.

The Officers of the Theoretical Division are pleased to acknowledge the assistance of Mr. Sigmund Schuldiner and Dr. Cecil King in conjunction with the symposium on "Adsorption Phenomena at Electrode Surfaces" as well as the general sessions of the Division at the San Francisco meeting.

ERNEST YEAGER, *Chairman*

1956 Extended Abstracts

The Electronics Division has available copies of the "Enlarged Abstracts" booklet, "printed but not published," containing 1000-word abstracts of papers presented at the Division's symposia on Luminescence and Semiconductors at the San Francisco Meeting of the Society, April 29–May 3.

The booklets are available at $2.00 each from:

Martin F. Quaely
Research Dept., Lamp. Div.
Westinghouse Electric Corp.
Bloomfield, N. J.

* * *

The Theoretical Electrochemistry Division also has available copies of the extended abstracts booklet of papers presented at the sessions of the Theoretical Division at the San Francisco Meeting of the Society. The booklet also contains abstracts of papers presented at the Symposium on "Adsorption Phenomena at Electrode Surfaces" sponsored jointly by the Theoretical Electrochemistry and Corrosion Divisions.

Copies can be obtained at $2.00 each from:

Ernest Yeager
Dept. of Chemistry
Western Reserve University
Cleveland 6, Ohio

SECTION NEWS

Cleveland Section

At the May 18 meeting, the following were installed as officers of the Section for 1956–57:

Chairman—K. S. Willson
Vice-Chairman—P. S. Brooks
Treasurer—R. A. Powers
Secretary—D. E. Kinney, 26550 Euclid Ave., Cleveland 32, Ohio

P. S. BROOKS, *Secretary (1955–56)*

New York Metropolitan Section

The annual Ladies' Night meeting was held May 23. There were 31 ladies present and, as usual, door prizes, favors, and orchids were provided for them.

The speaker for the evening was Mr. Ephriam Freedman whose talk was entitled "Behind the Scenes in Macy's Bureau of Standards."

In 1927, Jesse Isidor Strauss, President of Macy's, believing it was their function to act as purchasing agent for the community rather than as sales agent for manufacturers, asked Mr. Freedman to set up Macy's Bureau of Standards. The functions of this bureau were to examine offerings of manufacturers, substantiate manufacturers' claims, test goods for quality and serviceability, pass on customer complaints, and set up standards for merchandise. The first work undertaken by the bureau was the testing of fabrics; now a wide variety of materials is tested. Mr. Freedman said that because of the diversity of the work they probably are not experts in any field of testing. Since the bureau was started, much has been done to set up standards in various areas of industry. Much remains to be done in the way of setting up definitions and standards.

The talk was illustrated with a group of interesting slides. A lively question period followed.

KENNETH B. MCCAIN, *Secretary-Treasurer*

Pittsburgh Section

The Pittsburgh Section had its annual June symposium on June 8 at the new Westinghouse Research Labs. About 50 members of the Section took part in the proceedings.

A business meeting was held after the luncheon. The following were elected officers for the year June 1956 to June 1957:

Chairman—A. J. Cornish
Vice-Chairman—J. J. Stokes, Jr.
Secretary - Treasurer — Ling Yang, Metals Research Lab., Carnegie Institute of Technology, Pittsburgh 13, Pa.
Representatives on Council of Local Sections—E. A. Gulbransen and R. A. Woofter

A. J. CORNISH, *Chairman*

Washington-Baltimore Section

The following recently were elected officers of the Washington-Baltimore Section:

Chairman—D. T. Ferrell, Jr.
Vice-Chairman—Jeanne Burbank
Treasurer—David Schlain
Secretary—Gwendolyn B. Wood, National Bureau of Standards, Chemistry Bldg., Rm. 115, Washington 25, D. C.

JEANNE BURBANK, *Vice-Chairman*

NEW MEMBERS

In June 1956 the following were approved for membership in The

By action of the Board of Directors of the Society, commencing January 1, 1956, all prospective members must include first year's dues with their applications for membership.

Also, please note that, if sponsors sign the application form itself, processing can be expedited considerably.

Electrochemical Society by the Admissions Committee:

Active Members

GEORGE B. ADAMS, JR., Dept. of Chemistry, University of Oregon, Eugene, Ore. (Corrosion)

ADAM P. BANNER, Dow Chemical Co.; Mail add: 1407 Haley, Midland, Mich. (Corrosion)

MAURICE O. BARR, Associated Lead & Zinc Co.; Mail add: 5202 Ebell St., Long Beach 8, Calif. (Battery)

BRIAN E. CONWAY, Harrison Lab., University of Pennsylvania, Philadelphia 4, Pa. (Corrosion, Electrodeposition, Theoretical Electrochemistry)

LLOYD G. DEAN, Dow Chemical Co., Bldg. B-1220, Plant B, Freeport, Texas (Electrothermics & Metallurgy, Industrial Electrolytic)

WINSTON H. DUCKWORTH, Battelle Memorial Institute, 505 King Ave., Columbus, Ohio (Electrothermics & Metallurgy)

THOMAS P. HOAR, University of Cambridge; Mail add: 26 Storeys Way, Cambridge, England (Corrosion, Electrodeposition, Electrothermics & Metallurgy, Theoretical Electrochemistry).

RUSSELL D. JOHNSON, JR., Metallurgical Lab., Dow Chemical Co., Midland, Mich. (Corrosion, Electrodeposition, Theoretical Electrochemistry)

CLARENCE J. LENTZ, Quebec Iron & Titanium Corp.; Mail add: Box 40, Sorel, Que., Canada (Electrothermics & Metallurgy)

BIRKE M. LUCKENBILL, Morris P. Kirk & Son, Inc., 2717 S. Indiana St., Los Angeles 23, Calif. (Battery)

JAMES L. NICHOLS, Dow Chemical Co.; Mail add: 3701 Dartmouth Court, Midland, Mich. (Corrosion)

WILLIAM W. SMITH, Exide Industrial Div., Electric Storage Battery Co.; Mail add: 9200 Stenton Ave., Philadelphia 18, Pa. (Battery)

ETIENNE SPIRE, L'Air Liquide, Institut Recherches de la Siderurgie; Mail add: 3877 Draper Ave., Montreal, Que., Canada

JOHN R. THOMAS, Dewey & Almy Chemical Co.; Mail add: 62 Whittemore Ave., Cambridge 40, Mass. (Battery)

Student Associate Members

ROLF, T. SKRINDE, Massachusetts Institute of Technology, Rm. 1-083, Cambridge 39, Mass. (Corrosion)

Associate Members

(Awarded by the San Francisco Section)

EUGENE J. FENECH, University of California; Mail add: 2200 Mountain Blvd., Oakland 11, Calif. (Corrosion, Electrodeposition, Theoretical Electrochemistry)

WILLIAM S. HARRIS, University of California; Mail add: 2537 Etna, Berkeley 4, Calif. (Electrodeposition, Theoretical Electrochemistry)

ECS Membership Statistics

The following two tables give breakdown of membership as of July 1, 1956. 61 delinquents were removed from the rolls as of May 1, 1956. The Secretary's Office feels that a regular accounting of membership will be very stimulating to membership committee activities. In Table I it should be noted that the totals appearing in the right-hand column are *not* the sums of the figures in that line since members belong to more than one Division and, also, because Sustaining Members are not assigned to Divisions. But the totals listed are the total membership in each Section. In Table I, Sustaining Members have been credited to the various Sections.

TABLE I. *ECS Membership by Sections and Divisions*

Section	Division												
	Battery	Corrosion	Electric Insulation	Electrodeposition	Electronics	Electro-Organic	Electrothermics & Met.	Industrial Electrolytics	Theoretical Electrochem.	No Division	Totals as of 7/1/56	Totals as of 1/1/56	Net Change
Chicago	10	35	2	45	17	8	12	14	21	19	109	105	+4
Cleveland	48	36	3	47	36	13	19	26	41	13	181	171	+10
Detroit	6	17	5	37	5	7	4	3	20	20	83	73	+10
India	4	1	1	11	1	4	3	10	6	3	23	23	0
Midland	5	12	0	3	2	2	6	15	7	4	38	38	0
New York	64	98	19	130	80	27	52	58	77	71	444	427	+17
Niagara Falls	7	20	1	19	2	5	59	52	17	24	151	141	+10
Pacific Northwest	5	14	0	11	1	2	7	12	12	6	50	40	+10
Philadelphia	20	32	3	38	45	16	19	14	14	28	159	160	−1
Pittsburgh	3	38	3	22	14	5	26	13	30	8	100	85	+15
San Francisco	7	11	2	13	13	4	10	17	14	5	52	43	+9
Washington-Baltimore	33	39	9	32	19	3	10	10	28	7	114	108	+6
Ontario-Quebec	8	13	0	13	1	3	22	22	6	12	63	59	+4
U. S. Non-Section	67	119	25	121	69	44	82	83	127	82	518	622	−104
Boston	5	22	4	29	22	9	10	8	16	8	89	0	+89
Southern Calif. & Nevada	9	13	0	16	8	4	8	10	11	3	53	0	+53
Foreign Non-Section	36	41	8	49	20	24	28	53	51	53	183	175	+8
Total as of July 1, 1956	337	561	85	636	355	180	377	420	498	366	2410		
Total as of Jan. 1, 1956	309	518	88	609	312	172	341	401	476	377		2270	
Net Change	+28	+43	−3	+27	+43	+8	+36	+19	+12	−11			

TABLE II. *ECS Membership by Grade*

	Total as of 7/1/56	Total as of 1/1/56	Net Change
Active	2142	2013	+129
Life	14	14	0
Emeritus	37	34	+3
Associate	43	49	−6
Student	56	53	+3
Honorary	5	5	0
Sustaining	113	102	+11
Total	2410	2270	+140

Deceased Members Reported During May 1956

ROBERT W. BUZZARD, Washington, D. C.

PERSONALS

GEORGE A. PERLEY, widely known chemical engineer, retired on June 1

as Associate Director of Research of the Leeds & Northrup Co., Philadelphia, Pa. He joined the company in 1929 as Chief, Chemical Div., Research Dept., becoming Associate Director in 1951.

B. B. Dey has joined the Central Electro Chemical Research Institute, Karaikudi, India, as Honorary Director. It was not possible for B. K. Ram Prasad to take the appointment as Director.

G. Stuart Krentel has been appointed Manager of Technical Sales Service for the western region of Kelite Products, Inc., manufacturers of industrial cleaners and cleaning equipment. Mr. Krentel had been associated with several prominent organizations in the metal finishing field prior to joining the Kelite organization.

Alfred M. Pommer received the Ph.D. degree from Georgetown University, Washington, D. C., on June 11. He is continuing in his present employment as Chemist, U. S. Geological Survey, Washington, D. C.

Forbes S. Sibley, in February, left the Dow Chemical Co., Midland, Mich., to take a position in the Research Dept. of the Hoskins Manufacturing Co., Detroit.

Ernest G. Enck and William M. Raynor have been named Director of Planning and Director of Purchases, respectively, of Foote Mineral Co., Philadelphia, Pa., effective May 28. Dr. Enck retains his title of Secretary of the company but relinquishes his position as Director of Purchases in assuming his new duties. Mr. Raynor served as Manager of Special Products and as Administrative Assistant before receiving his new assignment.

ROBERT W. BUZZARD

Robert W. Buzzard, a project leader for the Metallurgy Div. of the National Bureau of Standards, Washington, D. C., died on May 3 at Ames, Iowa.

Born in Fenton, Mich., in 1904, Mr. Buzzard attended Michigan State College from which he received the B.S. degree in chemical engineering and in metallurgical engineering. After graduation he was briefly employed in Detroit and with the Navy Dept. before joining the Metallurgy Div. of the Bureau of Standards in 1927. He worked on the development of anodic coatings for the protection of aluminum and magnesium alloys against corrosion, for which he obtained several patents. He also published papers on the spark testing of steels and on hydrogen embrittlement of steel.

His scientific research was interrupted by military service in the Ordnance Corps in World War II. He served in the African and European theaters and was awarded the Bronze Star prior to his discharge.

After his discharge from service, Mr. Buzzard returned to the National Bureau of Standards and later supervised research on the development of constitution diagrams of interest to the Atomic Energy Commission. His latest interests had been in the development of a unique approach to alloying theory by means of an ionic analysis method.

In addition to The Electrochemical Society, he was a member of the American Society for Metals, the American Institute of Mining and Metallurgical Engineers, the British Institute for Metals, the Army Ordnance Association, and Alpha Chi Sigma.

1956 Directory

The 1956 Directory of Members of the Electrochemical Society should be available the latter part of August, rather than the latter part of July as stated in the July Journal. The Directory contains an alphabetical and geographical list of members of the Society as of March 1, 1956, and a list of Patron and Sustaining Members, Past Presidents, and winners of Society prizes and awards.

Members who wish to receive the Directory are requested to fill in and return the order form below, accompanied by check, to Society Headquarters, 216 West 102 St., New York 25, N. Y.

Please send_____copy(ies) of the 1956 Membership Directory to:

Name_____

Company_____

Street_____

City_____ Zone____ State_____

Attached is check for $_____ for Directory. (Single copies cost $2.00.)

NEWS ITEMS

New Sustaining Members

American Metal Co., Ltd., New York, N. Y., Gillette Safety Razor Co., Boston, Mass., and Weirton Steel Co., Weirton, W. Va., recently became Sustaining Members of the Society.

1956 Perkin Medal to Britton

Edgar C. Britton, Director of the Edgar C. Britton Research Lab. of the Dow Chemical Co., Midland, Mich., and Past President of the American Chemical Society, will receive the 1956 Perkin Medal of the American Section of the Society of Chemical Industry at a meeting of the Section following a dinner in his honor in the Grand Ball Room of the Waldorf Astoria in New York on September 14.

The 1956 award will be the 50th impression of the Perkin Medal, the highest honor in American industrial chemistry. It is bestowed annually for outstanding achievement in applied chemistry in the United States, and commemorates the discovery of the first synthetic dye by Sir William Henry Perkin in 1856. Presentation of the medal this year forms part of the celebration of the centenary of Perkin's achievement.

Young Author's Prize

At the Annual Banquet held on Tuesday evening, May 1, during the San Francisco Meeting of the Society, the Young Author's Prize of $100 was awarded to Milton Stern, Metals Research Labs., Electro Metallurgical Co., Niagara Falls, N. Y., for his two papers "The Electrochemical Behavior, Including Hydrogen Overvoltage, of

Iron in Acid Environments" and "The Effect of Alloying Elements in Iron on Hydrogen Overvoltage and Corrosion Rate in Acid Environments" which appeared in the November and December 1955 issues of the JOURNAL, respectively.

Dr. Stern received his B.S. degree in chemical engineering from Northeastern University and was awarded the Sears B. Condit Honor Award and the Nuodex Award upon graduation. After serving in the U. S. Navy as an electronics technician, he received an S.M. and Sc.D. degree in physical metallurgy from the Massachusetts Institute of Technology where he was an Aluminum Co. of America Fellow. He was associated with the Corrosion Lab. at M.I.T. from 1948 to 1954 and was Weirton Post-Doctoral Fellow from 1952 to 1954. Dr. Stern is now a research metallurgist at the Metals Research Labs. of the Electro Metallurgical Co., a Division of the Union Carbide and Carbon Corp.

Turner Memorial Award

J. G. Jewell, Gulf Research and Development Co., Pittsburgh, Pa., is the winner of the Francis Mills Turner Memorial Award, Sponsored by the Reinhold Publishing Corporation, consisting of $100 worth of books. His paper entitled "A Theoretical Basis for a New Method of Investigating Corrosion Inhibition" appeared in the April 1955 JOURNAL.

He received his B.S. degree in chemical engineering from The Rice Institute in 1945 and his M.S. in chemical engineering from Cornell University in 1947. For the past four years he has been a night-school student at the University of Pittsburgh in the Dept. of Mathematics.

Since 1947, Mr. Jewell has been with the Gulf Research and Development Co. doing research on corrosion and on petroleum-production problems. At present he is the head of the Corrosion Section of the Materials Engineering Division.

Gilbert Succeeds Bretschger as President of Becco Div.

Frederick A. Gilbert has been elected President of Becco Chemical Div. of Food Machinery and Chemical Corp., succeeding Dr. Max E. Bretschger who retired May 1 on the 30th anniversary of his association with the company.

Dr. Bretschger's retirement from the presidency comes at the peak of a brilliant career in the chemical world. During 1955 he was able to announce to the industrial world that "the thing that couldn't be done"—the production of 100% Hydrogen Peroxide—had been accomplished and the product was ready for shipment from the Becco plant in quantities from a pound to a tank car.

Mr. Gilbert came to Becco (Buffalo Electro-Chemical Co. at that time) as a control chemist in 1935. He later worked in the Research Lab. and the Production Dept. He assumed management and instituted operation of Becco's new peroxygen chemicals plant at Vancouver, Wash., in 1951. Two years later he returned to Buffalo as Assistant to the Vice-President; became Vice-President and Assistant Division Manager when Buffalo Electro-Chemical Co. was merged with Food Machinery and Chemical Corp., before his recent election to the presidency.

Pennsalt Expands Operations in Mexico

As an integral part of its projected five-year growth program, the Pennsylvania Salt Manufacturing Co. has announced further expansion of its operations in the Republic of Mexico. Nearing completion at Navojoa, Sonora, in the northwestern area, is a new agricultural chemical processing plant and distribution center.

Recently, Minerales y Metales Industriales, another subsidiary in Mexico, completed its first year of fluorspar mining activities in the San Luis Potosi area. Largest of its type in Mexico, this mine produces metallurgical grade ore used as a flux in making open hearth steel.

Carrier Engineering Scholarships

Scholarships for mechanical engineering study at four selected colleges have been announced by the Carrier Foundation, Inc., of Syracuse, N. Y.

The 1956 Carrier Scholarships will be awarded for the five-year course at Cornell University and for the four-year terms at Georgia Institute of Technology, Rensselaer Polytechnic Institute, and University of Kentucky. The award is $750 each year, which can be used by the winners for normal college expenses.

Instituted last year, four scholarships will be awarded annually to deserving young high school graduates who require financial assistance in order to secure a college education. Four students are currently completing their freshman year as Carrier Scholars at Cornell, Kentucky, Purdue University, and Syracuse University.

Scholarship applications by high school students interested in mechanical engineering careers should be made directly to the four colleges involved, which are responsible for selections in accordance with their established scholarship procedures. Carrier Scholars are required to maintain a position in the top third of their class.

Positive Temperature Coefficient Thermistors

Successful fabrication of thermistor materials having positive temperature coefficients as large as 14% was revealed recently by two Bell Telephone Labs. engineers speaking at the IRE-RETMA-AIEE-WCEMA Electronic Components Symposium in Washington, D. C. Most thermistors have negative coefficients. Harold A. Sauer and Steward S. Flaschen discussed the preparation of materials consisting of barium titanate or barium-strontium titanates to which small amounts of lanthanum have been added.

Bound Vol. 102 Available

Copies of bound Vol. 102 (1955) of the JOURNAL are available from Society Headquarters, 216 W. 102 St., New York 25, N. Y.

The Price is $12.00 to members of the Society and $18.00 to nonmembers.

Volumes Wanted

Will anyone who has a copy he no longer needs of Vol. 57 (1930), 62 (1932), 67 and 68 (1935) of the TRANSACTIONS of The Electrochemical Society please contact Bill F. Rothschild, Federal-Mogul Div., Federal-Mogul-Bower Bearings, Inc., 2355 Stadium Blvd., Ann Arbor, Mich.

U. S. Investors Participate in Israel Chemical Plant

A $3,000,000 chemical plant, established in Israel with American and European capital, know-how, and equipment, began operations recently. The plant produces chlorine, caustic soda, and a number of related chemicals essential to industry and agriculture, for both domestic and export requirements. It was established by

Electrochemical Industries (Frutarom) Ltd., which is affiliated with Palestine Frutarom Ltd., Haifa, manufacturers of essences, essential oils, and aromatic chemicals for the past 23 years.

Nearly half of the $3,000,000 investment came from a group of American businessmen who, in 1953, formed the American Electrochemical Industries, Inc., of Cleveland, Ohio, for the purpose of investing in the Israel venture.

Annual output of chlorine and caustic soda, which are produced by electrolysis of common salt, will amount to 2700 and 3000 tons, respectively.

Dow Chooses Site for Administration Center

Plans to build a new Administration Center in Midland, Mich., have been announced by the Dow Chemical Co. Starting this summer, the first three units to be constructed will consist of a Chemical Sales and Technical Service Bldg., an Executive Office Bldg., and a Plastics Bldg. In its final form the Center will cover an area almost ½ mile long and ¼ mile wide, and will contain headquarters for the entire company.

Pennsalt Improvements in Chemical Production

Officials of the Pennsylvania Salt Manufacturing Co. have announced intention to immediately replace sodium chlorate cells at the company's Portland, Ore., plant. Utilizing an improved electrolytic cell developed by Pennsalt technical and operating personnel, the new facilities are expected to go on stream early next year.

Company spokesmen pointed out that this improvement project is part of a $55,000,000 "program for future growth" which Pennsalt inaugurated late last year. Projects previously announced include plant expansions at Tacoma, Wash.; Wyandotte and Riverview, Mich.; Calvert City, Ky.; and Paulsboro, N. J.; the development of a fluorspar mine in Kentucky, and solar salt-harvesting facilities in Utah.

"Flame Ceramics" Coatings

Continental Coatings Corp., Chicago, has been granted exclusive license to the "Flame Ceramics" process developed by the Armour Research Foundation of Illinois Institute of Technology for the application of ceramic coatings to base materials.

Flame Ceramics coatings are produced by spraying nonmetallic powders through a flame gun (on which patents are pending) on an otherwise unheated surface, and can be applied to most metals, glass, carbon, and refractories. The coatings, generally crystalline oxides or oxide mixtures, are distinguished by their remarkable resistance to heat, abrasion, and chemical attack.

A number of coatings are available, including such materials as stabilized zirconium oxide, and uses for them vary widely, dependent upon the specific properties of each coating.

BOOK REVIEWS

ELECTROCHEMISTRY IN BIOLOGY AND MEDICINE. Edited by Theodore Shedlovsky. Published by John Wiley & Sons, Inc., New York, 1955. xii + 369 pages, $10.50.

Phase boundaries are a matter of life or death in the functioning of living things. Each cell of an organism—whether the single one of an amoeba, or one of billions in the human—is bounded by a membrane. Other types of interfaces separate intracellular components from their liquid matrix of the living protoplasm, and sheets of cells line or cover organs (lungs, integument, intestines, uterus, etc.). At all of these boundaries highly selective processes must be maintained for life to go on. They determine, e.g., transport of food substances into the living stuff and of wastes out of it; and especially at the bounding membranes of nerve and muscle cells occur the "impulses" without which the activation of a littlest finger movement, or a heart beat, or the grandest achievement of an Einstein or a Mozart would be impossible.

As at all phase boundaries, so at biological ones, electric potentials develop. This basic feature is the main concern of the book under review, which puts into published form the proceedings of the Symposium on Electrochemistry in Biology and Medicine that was organized by Dr. Shedlovsky and held in 1953 during the 103rd Meeting of The Electrochemical Society. As stated in Dr. Shedlovsky's preface: "The subjects covered include discussions from several points of view of membranes, nerve and plant cells, biologically important ions, and applications of polarography, electrocardiography, and electroencephalography in medicine. The contributing authors are active scientific investigators whose chapters in this volume are based largely on their own experimental work in the fields they discuss. Among them are physicists, chemists, biologists, and medical men, yet they all share an interest in the difficult fundamental electrochemical problems of living processes." To this it should be added that all 19 papers, and even the detailed index of the book, are of the highest order of merit.

It would be impossible to summarize in this short review even a portion of the rich material this book presents to us, and in any case it would be invidious to do so. It is therefore desirable to point out only some highlights of general interest.

This book gives gratifying and new

DECEMBER 1956 DISCUSSION SECTION

A Discussion Section, covering papers published in the January–June 1956 JOURNALS, is scheduled for publication in the December 1956 issue. Any discussion which did not reach the Editor in time for inclusion in the June 1956 Discussion Section will be included in the December 1956 issue. Those who plan to contribute remarks for this Discussion Section should submit their comments or questions in triplicate to the Managing Editor of the JOURNAL, 216 W. 102nd St., New York 25, N. Y., *not later than September 1, 1956*. All discussions will be forwarded to the author, or authors, for reply before being printed in the JOURNAL.

testimony that the fundamental methods and theories of electrochemistry, and of both alternating current and transient analysis of purely electrical circuits, can be rigorously used in studies of biological interest. Some of these studies, such as those built around permselective collodion membranes, are concerned with highly simplified models of their living originals and thus involve the quite perfect control of experimentation that permits sound theoretical analysis. But many are performed directly on living structures, and, especially in those on single cells, there is little or no loss in finesse of technique or precision of thinking that characterizes the work of the pure physical chemist. Indeed, this book shows that, in their attempts to solve basic electrochemical problems of the cell membrane, biologists today, carrying on in the tradition of, e.g., Galvani, are opening up new fields of both experimental and theoretical interest. This point will be strikingly exemplified by reading of researches: on transmembrane potential differences (done with microelectrodes, with tips a fraction of a micron in diameter, that can be thrust without biological injury into the cell interior) which, among other fascinating things, inform us that the membrane withstands an electric field strength of the order of 10^5 v/cm (0.1 v across 10^{-6} cm); on nonlinear systems involved in generation of action potentials; on newly postulated systems (such as the catalytic one involving the enzyme, acetylcholinesterase) for conversion of chemical into electrical energy; and on the use of "membrane electrodes" for determination of activities of certain ions, such as sodium and ammonium, for which conventional electrodes do not exist, or are too difficult or limited to use.

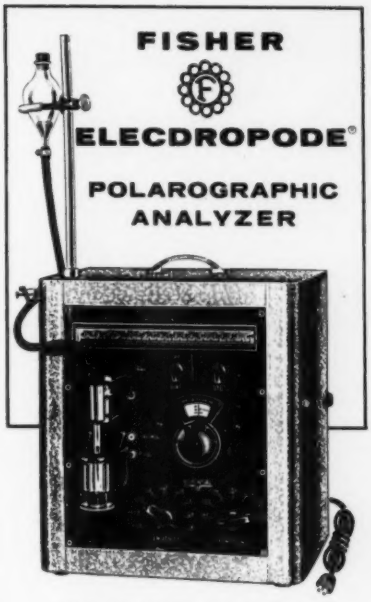
This book demonstrates another fact of great interest, the varied biological activities in which electrochemical mechanisms play a role. Obvious, of course, is the point that the living integrity of a cell, plant, or animal depends on the resting potential across its membrane, and that communication by nerve cells of intelligence from one part of the organism to another (which includes feedback devices in special cases) is largely performed by membrane localized, self-propagated action potentials. But it is also evident that transport across membranes of ions, or more generally all polar substances, is determined by electrochemical mechanisms, and that certain, and probably most, metabolic changes are electrochemical. Many more instances of this sort indicate the play of electrochemical reactions almost universally in biological activities, and that they are of interest not only for an understanding of basic properties of living systems, but also in medical practice. Although this book has a wealth of examples of this sort, it seems to this reviewer that it would have been still further enriched by some consideration of oxidation-reduction potentials and their role in metabolism, and the electromechanochemical reactions that are now being actively studied in relation to mechanisms of muscular contraction.

"Electrochemistry in Biology and Medicine" is an authoritative and important book. It deals with its subject both intensively and extensively; it bristles with the disciplined analytic methods of the physical chemist and the physicist (who, in some cases, may go by the name of "biologist" or "physiologist") and with revelations of the electrochemical complexities of living processes that help us to understand the nature of life itself. Any biologist or electrochemist, or any scientist, who wishes to be informed on electrochemistry in current biology and medicine should read this book. He will at least be struck by the thought that, whether or not "life hangs by a thread," it can certainly be said that it hangs by a membrane, and that in this vital dependence electrochemistry plays a critical role.

ALEXANDER SANDOW

SOLID STATE PHYSICS: ADVANCES IN RESEARCH AND APPLICATIONS. Edited by F. Seitz and D. Turnbull. Vol. I. Published by Academic Press, Inc., New York, N. Y., 1955. xii + 469 pages, $10.00.

This is the first volume of a series of a dozen or more, to appear semiannually at first, which are intended to treat the entire field of solid state physics. As the editors assert, covering the field at a sufficiently advanced level to be useful to those intending to work in it is impossible on a smaller scale, while the need for such an enterprise has grown with every fat issue of the *Physical Review*. The form and quality of this first volume augur well for the success of the project. It is to be hoped that the remainder of the considerable number of solid state physicists organized for the job will do as well.



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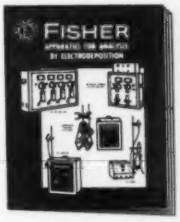

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This volume contains three articles organized around the problem of cohesion in solids: one by Pines treating electron plasma effects in metals, a related subject; and two more conventional review articles of the comprehensive type by Muto and Takagi on order-disorder and by Fan on silicon and germanium.

The first two of the cohesion articles are on a pedagogical level. The first, by Reitz, is essentially an up-to-date version of the central chapters, on the one-electron theory in solids, of Seitz's book, with extensive literature references. I found this clear and complete; I might have preferred some one real physical example, replacing some of the mathematical model calculations. The second, by Wigner and Seitz, is a slight revision of Wigner's article at the Japanese International Conference in 1953 and gives in a brief space some highly stimulating insights into cohesion in complicated metals. The article by Ham summarizes and extends the Harvard work on simplifying band calculations; it is more an expanded research paper than a review article, and it is unfortunate that time prevented its containing a more complete tabulation of final results. Nonetheless it represents what seems to be the final word as to methodology.

Next we have the order-disorder paper of Takagi and Muto. This is a highly useful paper, and I liked particularly the inclusion of discussions of interaction of order with other phenomena such as magnetism and resistivity. It seemed unfortunate that Kikuchi's work based on Takagi's own method was omitted, since it also is not covered in other recent reviews. More discussion of interaction with vibrations and of compositional asymmetry might also have been worthwhile.

Fan's article, like the previous one, cannot avoid the difficulty of standard review papers of very great condensation, but does manage to be reasonably complete and readable; it will be a valuable source both for experimentalists and theorists. Finally, Pines' article appears at an excellent time at which to summarize this new and rapidly expanding field. The later sections on the various applications of the work are very good; I, myself, would prefer more physical explantions of his transformations in the early part of the paper.

On the whole, this is a surprisingly good book, of much more consistent high quality than expected. Its primary function is to inform the worker with a serious interest in the particular subject; only a few of the articles will be of much help as general education. The present volume is primarily theoretical, but more experimental papers are to be expected in later ones.

One final point that might be mentioned is that any active solid state physicist will need to own several of these volumes. At $10.00 each the cost will be high. The situation can be alleviated, as it is in part in this volume, by grouping related articles together. However, it seems to me that the price per volume has been set high considering that it probably will be in great demand.

P. W. Anderson

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